THE DISTRIBUTION OF OXYGEN-CONTAINING FUNCTIONAL GROUPS IN PITCH FROM A HIGH-TEMPERATURE COAL TAR

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INTRODUCTION

The phenolic hydroxyl content of coal tar pitch is mainly confined to the portion insoluble in light petroleum. In this portion there is approximately one phenolic group per molecule of pitch constituent - indicating that the phenolic hydroxyl, although small in percentage, is a significant (1) constituent. It has been shown (2) that, for a series of pitch fractions prepared from coke-oven, vertical-retort, and low-temperature tars, 40 to 68 per cent of the oxygen in the benzene-soluble, light-petroleum-insoluble fractions and 28 to 63 per cent of the oxygen in the pyridine-soluble, benzene-insoluble fractions is in the form of phenolic groups.

The present paper describes a systematic study of the oxygen-containing groups in a pitch from a high-temperature tar obtained by carbonizing a medium-volatile bituminous coal at 1000°C. in a technical-scale plant simulating conditions in a by-product coke-oven. An attempt has been made to account for all the oxygen, other than ethereal oxygen, in the pitch and to relate the concentration of the various functional groups to the molecular size of the pitch fraction.

EXPERIMENTAL

A. Preparation of Pitch and Pitch Fractions

A pitch of softening point 66°C. (K. and S.) was prepared by rapid distillation (70 grams per minute) of a 5-kilogram charge of tar in a metal still of the S.T.P.T.C.* type - a method believed to yield a pitch similar to those produced industrially in pipe stills (3).

The pitch was separated into four fractions by solvent extractions:

(i) "Crystalloids" - soluble in light petroleum (b.p. 60 to 80°C.).

(ii) "Resinoids" - insoluble in light petroleum but soluble in benzene.

(iii) "C_2" - insoluble in benzene but soluble in pyridine.

(iv) "C_1" - insoluble in pyridine.

The C_2 fractions were further separated by fractional precipitation of a pyridine solution of the C_2 with water.

All separations and functional-group analyses were carried out in darkness and in an atmosphere of nitrogen.

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* Standardization of Tar Products Tests Committee (Great Britain).

B. Determination of Functional Groups

1. Phenolic Groups

I. Non-aqueous titration. - Mixtures of the sample (0.1 to 0.5 gram) with 2,6-xylenol (0.01 to 0.02 gram) were titrated potentiometrically in pyridine solution (or suspension) with 0.2N sodium aminoethoxide in ethylene diamine as described by Greenhow and Smith (4). By co-titration with xylenol it is possible to estimate phenolic groups not normally giving a sharp end point in the absence of this reagent, but in addition the method gives an estimate of the carboxyl, phenolic ester, phenolic lactone, and some quinone groups. Carbon dioxide and carboxylic acids give a separate inflexion in the titration curve (4), and may be allowed for; the inflexion is sharpened by the addition of benzoic acid to the sample (see 3, II below). Titrations were reproducible within 10 per cent.

II. Mesylation. - The sample (0.8 to 1 gram) in pyridine (50 ml.) was treated at 0 to 5°C. with freshly distilled methane sulphonyl chloride (7 ml.) for about 24 hours, the mixture poured into ice water (200 ml.) and acidified with 5N hydrochloric acid, the precipitate washed with 5N hydrochloric acid and, finally, with water, and dried in vacuo at 50°C. The hydroxyl content was measured from the increase in sulphur content of the sample; reproducibility was about four per cent. It was found that various pure compounds, including heterocyclic tertiary amines, quinones, esters, lactones, and carbazole derivatives, did not react with methane sulphonyl chloride under the conditions used. A low mesylation value was obtained with indole, probably by the addition of part of the reagent molecule to chains of indole polymer. Primary amines, secondary aliphatic amines, and alcohols react to give the expected mesyl derivatives.

III. Methylation. - Diazomethane in ether was used as the reagent, a 1:1 mixture of dry ether and benzene as the solvent for the pitch fraction, and methanol as the catalyst. The methylated product was separated into two fractions, one being insoluble and the other soluble in the reaction medium. Methoxyl determinations were carried out on the methylated sample before and after hydrolysis (with N hydrochloric acid) for measurement of the carboxylic acid content.

IV. Acetylation. - The technique used was that of Blom et al. (5) in which the sample is first treated with acetic anhydride in pyridine, the acetylated product is then hydrolysed with barium hydroxide, and finally the acetic acid is distilled from the acidified solution and titrated. The acetic acid distilled irregularly from hydrolysed acetylated crystalloids and resinoids, indicating that further hydrolysis, possibly of N-acetyl compounds, was taking place in the acid solution.

V. Methylation followed by acetylation. - Processes III and IV were used, in series.

VI. Acetylation followed by methylation. - Processes IV and III, in that order.

2. Carbonyl Groups

The method used was that of Blom et al. (5), in which hydroxylamine hydrochloride is the reagent. Oxime formation was measured in three ways, namely from (i) the increase in nitrogen content, (ii) the decrease in nitrogen content on hydrolysis of oxime, and (iii) determination of hydrolysable oxime as ammonia. Application of the method to pitch samples gave a reproducibility of about eight per cent.

3. Carboxylic Acids

These were determined by the hydrolysis of methylated samples (1, III above) and by two additional methods:

I. Decarboxylation. - A semi-micro procedure similar to that of Beroza (6) was used but with a larger sample (0.4 gram instead of 0.05 to 0.1 gram) because of the low carboxylic acid content of the pitch fractions. Reproducibility was about four per cent.

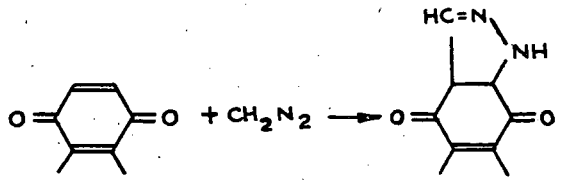
II. Non-aqueous titration. - A mixture of the sample (0.3 to 0.8 gram) with benzoic acid (0.015 to 0.025 gram) was titrated potentiometrically using the same solvent, titrant, and electrodes as in Method 1, I (above); the first major inflexion was taken as the end point. Reproducibility was about ten per cent.

4. Ester Groups

The method employed by Knotnerus (7) for the determination of the saponification number of blown bitumens was adopted. Reproducibility was poor (about twenty per cent), probably because of the low solubility of the pitch fractions.

5. Quinones

It is probable that much of the oxygen measured in the carbonyl determination is quinonoid. The increase in nitrogen content of samples following treatment with diazomethane could also be attributed to quinones - but only to 1,4-quinones of the types known to undergo addition with diazomethane to form pyrazoline rings (8, 9) - that is, "terminal ring" quinones:



A value for 1,4-quinones can therefore be calculated from the uptake of nitrogen.

C. Molecular Weights and Coking Values

Molecular weights were determined cryoscopically in phenanthrene, and coking values by the method of Charette and Girolami (10).

RESULTS AND DISCUSSION

The solvent analysis of the pitch, the elementary analysis and coking values of the pitch and pitch fractions, and the molecular weights of the soluble fractions, are given in Table I. This shows that the percentage of oxygen tends to be higher in the less-soluble fractions of the pitch, and that decrease in solubility is accompanied by increase in molecular weight and coking value.

Table II summarizes the functional group analyses of the pitch fractions; values tabulated are the average of at least two determinations.

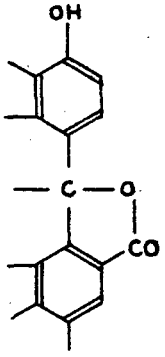
Close agreement for phenolic hydroxyl determined by non-aqueous titration and by mesylation was obtained for the crystalloids and the resinoids. The values for functional groups in the C_1 fraction are generally low (Table III), probably because of its insolubility. In this case the mesylation hydroxyl value is higher than the titration value and this may be due to the greater reactivity of the methane sulphonyl chloride or to the longer reaction time employed.

In comparison with the other techniques, methylation and acetylation gave lower values for phenolic hydroxyl.

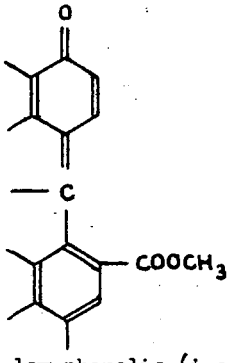
When methylated fractions were acetylated, higher overall hydroxyl values

were obtained than when either acetylation or methylation was used alone. On the other hand, when acetylated fractions were methylated, values were obtained similar to those with methylation alone, and infra-red examination of the methylated acetylated products revealed that all the acetyl groups had been eliminated. This elimination reaction was noted for pure compounds by Bredereck et al. (11). Results obtained by acetylation of methylated fractions suggest that methylation may make functional groups more accessible to acetic anhydride. Several types of hydroxyl groups appear to be present, probably of different acidities and/or steric disposition.

Carboxylic oxygen in the resinoids and C_2 determined by hydrolysis of methylated fractions is higher than that measured by decarboxylation or non-aqueous titration, and is highest in the C_2 fraction. High carboxyl and low hydroxyl (by methylation) values could be explained by lactones of the fluorescein type (12).



which, on treatment with diazomethane, give an ester



Such a reaction could account for the low phenolic (i.e. hydroxyl) values obtained with the C_2 fraction.

Bearing in mind the relatively low accuracy of the decarboxylation and titration methods it is probable that the carboxylic acid contents of the resinoid and crystalloid fractions are negligible, and the methylation value for the resinoid fraction would again be due to the presence of lactones. The fact that there was little difference in the values given by these two methods for the carboxylic-acid content of the C_2 fraction, indicates that these values are significant.

The resinoid and C_2 fractions had the highest carbonyl contents. The three methods of measuring the extent of reaction with hydroxylamine gave similar results, indicating that nitrogen uptake was entirely in the form of hydrolysable oxime.

Calculation of 1,4-quinone oxygen from the nitrogen increase following methylation has given values lower than those for carbonyl oxygen (except with crystalloids), but of the same order. The results could be interpreted to mean

that much of the carbonyl is in the form of terminal-ring 1,4-quinones.

Diazomethane also forms pyrazolines with $\alpha\beta$-unsaturated ketones and aldehydes (8); but in the present investigation it is assumed that these are absent from high-temperature tar.

Ester groups appear to be absent from all fractions except the resinoid, which latter has an "ester-oxygen" content approximately equivalent to the content of carboxylic-acid oxygen measured by the hydrolysis of the methylated resinoids. This evidence supports the suggestion that methylation of a lactone had occurred.

Oxygen, as phenolic hydroxyl (by mesylation), carbonyl (by oxime formation), and carboxyl (by decarboxylation) is given as a percentage of the total oxygen (determined by the direct method) in Table III. It can be seen that for the resinoids the total functional-group oxygen is higher than, and for the crystalloids and C_1 fraction lower than, the total oxygen; while for the C_2 fraction the total functional-group oxygen is approximately the same as the total oxygen. The high value for functional-group oxygen in the resinoids could be explained, partly at least, by the possibility that mesylation will determine other groups in addition to phenolic ones. Non-aqueous titration - which gives the same value as mesylation - can determine certain terminal-ring, 1,4-quinones as "phenolic hydroxyl". The extent of such overlapping as this between the methods employed for functional-group analysis is difficult to estimate, and at present an approximate figure cannot be given for unreactive (i.e. ethereal) oxygen, although consideration of the results as a whole suggests that this should be low for the resinoids and the C_2 fraction.

The C_2 is the fusible fraction of highest molecular weight obtained by the solvent-extraction method used in this work, and it gives the highest yield of coke (C_1, being infusible, gives a char). Van Krevelen et al. (13) have shown that free carbon ($C_1 + C_2$) of pitch is similar to a coking coal in its dilatometric properties, so that the C_2 probably contains the more important coking constituents of pitch.

The present authors have separated the C_2 into three parts by fractional precipitation of its pyridine solution with water (Table IV). As expected, the least soluble part had the highest molecular weight (832) and the most soluble the lowest (420). However, the coking values were similar for each part and the phenolic hydroxyl content was highest in the lowest molecular-weight fraction. Clearly, molecular size is not the only factor controlling either the insolubility of C_2 in benzene or its high coking value. Results so far show that functional groups, of which phenolic hydroxyl is probably the most important, play a part.

CONCLUSIONS

(1) The concentration of oxygen-containing functional groups is highest in the light-petroleum insoluble fractions and in particular in the C_2.

(2) Phenolic hydroxyl, carbonyl, and carboxylic acid groups account for most of the oxygen in the pitch fractions examined.

(3) Phenolic hydroxyl is the most important oxygen-containing functional group, whilst carbonyl oxygen and carboxylic-acid oxygen occur in approximately equal amounts except in the resinoid fraction, where the carbonyl oxygen is high (accounting for almost 50 per cent of the total) and the carboxylic-acid oxygen probably negligible.

(4) The content of ethereal oxygen is probably low in the resinoids and the C_2 fraction.

(5) The "insolubility" and high coking value of the C_2 fraction depend not only on

its high molecular weight but also on the presence of reactive centres, one of which is probably the phenolic hydroxyl group.

ACKNOWLEDGEMENTS

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TABLE I. ANALYSIS AND PROPERTIES OF PITCH AND PITCH FRACTIONS

Pitch Fraction	% Total Pitch	Elementary Analysis						Mol. Wt.	Coking Value, %
		C	H	O*	N	S	Ash		
Crystalloids	38.5	92.0	5.6	1.7	1.1	0.4	0.1	230	10.8
Resinoids	18.5	90.2	4.8	2.8	2.2	0.4	0.1	381	58.3
C_2	15.5	86.7	4.2	4.3	2.6	0.6	1.4	608	85.5
C_1	27.5	91.6	2.9	2.6	1.4	0.7	1.0	-	94.1
Pitch	100	91.4	4.5	2.4	1.3	0.5	0.5	-	56.6

* Direct method.

TABLE II. FUNCTIONAL GROUP ANALYSES

	Oxygen as Phenolic Hydroxyl, %						Oxygen as Carboxyl, %			Oxygen as Carbonyl, %	Oxygen as 1,4-Quinone, %	Oxygen as Esters, %
Method of Analysis / Fraction	Non-aqueous titration	Mesylation	Methylation	Acetylation	Methylation followed by acetylation	Acetylation followed by methylation	Methylation and hydrolysis	Decarboxylation	Non-aqueous titration	Oxime formation	Nitrogen content of methylated sample	Saponification
Crystalloids	0.90	0.95	0.36	0.54	0.75	0.46	< 0.1	0.19	< 0.1	0.25	0.41	nil
Resinoids	1.9	1.9	0.83	0.63	1.27	0.52	0.58	< 0.1	< 0.1	1.34	1.00	0.43
C_2	2.0	2.5	0.57	1.2	1.51	0.59	1.47	0.93	1.1	0.93	0.86	nil
C_1	0.55	1.2	0.57	0.49	0.95	0.64	0.26	0.60	0.50	0.44	0.39	nil
Pitch	-	2.1	0.39	0.96	-	-	0.25	0.23	-	0.53	0.35	-

TABLE III. FUNCTIONAL-GROUP OXYGEN AS PERCENTAGE OF TOTAL OXYGEN

Fraction / Functional Groups	Crystalloids	Resinoids	C_2	C_1
Phenolic hydroxyl (mesylation)	56	68	58	46
Carbonyl (oxime formation)	15	48	22	17
Carboxylic acid (decarboxylation)	11	3	22	23
Total	82	119	102	86

TABLE IV. PRECIPITATION PRODUCTS FROM C_2 FRACTION

Fractions	Yield, as % of C_2 Fraction	Colour	Mol. Wt.	Oxygen, as Phenolic Hydroxyl, %	Coking Value, %
$C_2/1$	46.6	Black	830	1.3	89.7
$C_2/2$	26.6	Dark brown	545	2.2	89.1
$C_2/3$	26.8	Reddish-brown	420	2.9	86.2

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR

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INTRODUCTION

In a previous publication[1] the Bureau of Mines reported the results of a detailed gas-liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature bituminous coal tar. The present work extends this detailed characterization to include compounds boiling up to 280°, specifically, compounds in the range 202° to 280°.

Previously, only about 10 aromatic hydrocarbons boiling between 202° and 280°, including naphthalene and 5 alkylnaphthalenes, were found in low-temperature tars and in all instances by older techniques[2-6]. Quantitative results were essentially non-existent.

In the present work, employment of the eminently effective combination of gas-liquid chromatography and spectrophotometry enabled this laboratory to identify 48 compounds, including 9 mentioned in the previous publication. Of these identified compounds 20 are alkylnaphthalenes, including all isomeric dimethylnaphthalenes, except the 1,8-isomer. The rest of the compounds identified include methylated indans, tetralins, indenes and biphenyls, and some oxygenated aromatic hydrocarbons. Cyclohexylbenzene and 2a,3,4,5-tetrahydroacenaphthene, which had never been reported in any low-temperature tar, were also found. Quantitative determinations were made on nearly all compounds.

A correlation between logarithm of relative retention at 220° and boiling point for some alkylbenzenes and some alkylnaphthalenes was established; this made it possible to identify several additional constituents of the tar. This correlation is similar to the one for alkylbenzenes at 150°[1].

EXPERIMENTAL WORK AND RESULTS

1. Preparation of aromatic concentrates from the coal tar for gas-liquid chromatography

The same neutral oil from a West Virginia bituminous coal tar that was used in the earlier part of this work was used for the present analysis. The neutral oil was distilled to the equivalent of 260° in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus at 50 mm., with the results shown in Table I of the previous publication. The residue left from this distillation was further fractionated at 10 mm. in a Fisher Unitized distillation apparatus with a 12 mm. I.D. column, using a reflux ratio of 20 to 1. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

The distillate fractions were each separated into saturates, unsaturates, and aromatics by means of displacement chromatography with silica gel, as previously described. The data on displacement chromatography are summarized in Table II.

TABLE I

FRACTIONATION OF NEUTRAL OILS IN FISHER STILL

Charge:	8.35 wt.-% of the tar	
	338.0 g.	
Distillate:	131.4 g.	= 38.9 %
Residue:	201.8 g.	= 59.7 %
Loss and holdup:	4.8 g.	= 1.4 %

Fraction No.	Head temperature, °C., 10 mm.	Estimated b.p., °C., 760 mm.	Weight, g.
1	122 - 124	257 - 259	2.9
2	124 - 127	259 - 262	9.0
3	127 - 129	262 - 265	9.0
4	129 - 132	265 - 268	9.3
5	132 - 134	268 - 270	8.5
6	134 - 135	270 - 272	6.2
7	135 - 137	272 - 274	9.2
8	137 - 138	274 - 275	9.6
9	138 - 139	275 - 276	9.0
10	139 - 141	276 - 278	9.0
11	141 - 143	278 - 280	8.6
12	143 - 144	280 - 282	9.4
13	144 - 146	282 - 284	9.2
14	146 - 148	284 - 286	9.3
15	148 - 149	286 - 287	9.6
16	149	287	3.6
		Total	131.4

TABLE II

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No.[a]	Weight of charge, g.	Column temperature, °C.	Saturates + some olefins			Aromatics + some olefins and some O, S compounds			Material retained on column, g.	Weight of aromatics identified by GLC, g.
			n_D^{20} range	Total weight, g.	Number of fractions	n_D^{20} range	Total weight, g.	Number of fractions		
7 + 8[b]	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11	1.99	5.828
9[b]	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7	0.58	1.329
10 + 11[b]	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13	1.53	3.152
12 + 13[c]	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13	1.71	3.089
14[c]	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13	0.75	2.314
15[c]	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18	1.04	5.419
16[c]	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18	1.98	5.771
17[c]	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15	2.77	4.322
18[c]	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12	1.07	4.665
19[c]	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13	2.72	4.647
20[c]	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11	2.02	3.672
21[c]	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16	1.23	5.989

(Table II, continued)

22[c]	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22	1.36	8.048
23[c]	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20	1.01	8.516
24[c]	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10	0.40	2.863
25[d]	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23	1.49	11.502
26[d]	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28	1.62	11.874
27[d]	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23	1.71	10.691
28[d]	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25	1.69	10.057
29[d]	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12	1.16	5.414
1*[d]	2.90	95	1.4698	0.40	1	1.5489-1.6015	2.30	6	0.20	1.436
2*[d]	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11	0.97	4.991
3*[d]	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7	0.78	2.931
4*[d]	7.66	95	1.4537-1.5048	2.01	4	1.5232-1.5978	4.84	8	0.81	2.870
5*[d]	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11	1.03	3.739
6*[d]	6.00	95	1.4587-1.4895	1.40	3	1.5189-1.5903	3.93	6	0.67	2.865
7*[d]	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8	0.47	2.773
8*[d]	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12	1.01	3.622

a Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report[1].
b Desorbent - butyl alcohol.
c Desorbent - isobutyl alcohol.
d Desorbent - cyclohexanol.

II. Analysis of aromatic hydrocarbons by gas-liquid chromatography

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer equipped with thermistor detectors was used. The response range of the recorder was from 0 to 2.5 mv, and the chart speed varied from 4 to 20 inches per hour, depending on the retention times of the components. The peak areas on the chromatogram were measured with a planimeter.

Two columns were used, each made from a 20-ft. x 1/4-in. O.D. copper tubing filled with approximately 75 g. of packing made of 25% Apiezon L grease on 30- to 60-mesh firebrick. One of the columns was used at 200°, which was the temperature chosen for the analysis of the fractions boiling between 202° and 233°. The other column was used at 220°, which was the temperature for the analysis of the fractions boiling between 233° and 275°. The samples varied in size from 5 µl to 15 µl and were injected into the column with a 50-µl syringe. The carrier gas was helium, admitted to the column at a pressure of 30 lb./in.^{2}, corresponding to a flow rate of 100 ml./min.; the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within ± 0.1° and the helium pressure and the voltage of the detector stayed constant.

The efficiency of the column was calculated by using the equation[7]: No. of theoretical plates = $16(x/y)^2$, where y = length of peak baseline (as defined) and x = length from start of the run to middle of baseline section. Referring to 1,3,5-triethylbenzene and to 1-methylnaphthalene, the efficiency of the column at 200° was 2393 and 3948 theoretical plates, respectively, and for the column at 220° was 3364 and 4356.

General approach for identification. The retention times of 58 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained. Their calculated relative retentions (either time or volume) referred to 1,3,5-triethylbenzene at 200° and 220°, and their boiling points are shown in Table III. The aromatic fractions obtained by displacement chromatography were each examined by GLC under the same conditions as for the known compounds.

The approach for identification was principally the same as that described in the previous paper, except that ultraviolet spectrophotometry was included in addition to infrared. Components producing peaks were collected in the previously described manner. The ultraviolet spectra were obtained in cyclohexane solutions.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. In some instances, two components were found to have been eluted together. The infrared spectrum of the material producing a single peak served not only for qualitative identification but also for quantitative estimation of the components. The chromatograms for two different aromatic cuts shown in Figure 1 illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table IV shows the results of the identifications, the peak numbers in this table corresponding to the peak numbers in Figure 1.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available. These correlation curves are shown in Figure 2 and are discussed more fully in a later section. Boiling points of the components producing various peaks were obtained from their

TABLE III

BOILING POINTS, RELATIVE RETENTIONS, AND CALIBRATION FACTORS (f_c) OF SOME AROMATIC HYDROCARBONS

Compound	Boiling point °C./760 mm.	Source	At 200° Relative retention[a]	At 200° f_c[b]	At 220° Relative retention[a]	At 220° f_c[b]
n-Propylbenzene	159.217	c	0.37	0.86	0.40	0.85
1-Methyl-2-n-propylbenzene	184.80	c	0.62	0.95	0.64	0.93
1,4-Diethylbenzene	183.752	c	0.58	0.93	0.61	0.93
1,3-Dimethyl-5-ethylbenzene	183.75	c	0.58	0.91	0.60	0.89
1,2-Dimethyl-4-ethylbenzene	189.75	c	0.67	0.94	0.70	0.92
1-Methyl-3,5-diethylbenzene	200.70	c	0.77	1.00	0.79	0.97
1,2,4,5-Tetramethylbenzene	196.80	c	0.82	0.98	0.84	0.98
1,2,3,5-Tetramethylbenzene	198.00	c	0.85	1.02	0.87	0.99
1,3,5-Triethylbenzene	216.2	c	1.00	1.00	1.00	1.00
Pentamethylbenzene	231.8	c	1.72	1.01	1.75	1.00
Hexamethylbenzene	263.8	d	3.58	1.01	3.47	1.01
Cyclohexylbenzene	240.13	e	2.09	1.03	2.05	1.02
1,2,3,4-Tetrahydronaphthalene	207.57	c	1.14	1.54	1.16	1.52
Indan	177.82	c	0.59	1.42	--	--
Naphthalene	217.96	c	1.35	1.02	1.37	1.03
2-Methylnaphthalene	241.14	f	2.12	1.04	2.10	1.02
1-Methylnaphthalene	244.78	f	2.32	1.01	2.28	1.02
2-Ethylnaphthalene	257.9	c	3.01	1.08	2.93	1.07
1-Ethylnaphthalene	258.67	c	3.04	1.05	2.96	1.05
2,7-Dimethylnaphthalene	262	c	3.21	1.07	3.13	1.05
2,6-Dimethylnaphthalene	261	f	3.28	1.03	3.17	1.04
1,7-Dimethylnaphthalene	262.9	e	3.41	1.03	3.29	1.03
1,6-Dimethylnaphthalene	265.5	e	3.54	1.04	3.43	1.02
1,3-Dimethylnaphthalene	265	c	--	--	3.43	--
2,3-Dimethylnaphthalene	268	f	3.80	1.05	3.68	1.03
1,5-Dimethylnaphthalene	270.1	e	3.99	1.03	3.83	1.03
1,2-Dimethylnaphthalene	271.1	g	4.10	--	3.93	--
1,3,7-Trimethylnaphthalene	281.7	e	--	--	4.88	1.09
2,3,6-Trimethylnaphthalene	288.1	g	--	--	5.51	1.09
2,3,5-Trimethylnaphthalene	289	e	--	--	5.66	1.07
2a,3,4,5-Tetrahydroacenaphthene	252	e	2.88	1.20	2.80	1.20
Acenaphthylene	270	d	--	--	4.05	--
Acenaphthene	277.2	f	--	--	4.53	1.12
Biphenyl	255.0	c	2.66	1.01	2.60	1.00
3-Methylbiphenyl	272.70	c	--	--	3.82	1.04
2-Methylbiphenyl	260	d	2.46	--	2.51	1.06
4-Methylbiphenyl	267	d	--	--	3.10	--
2-Methylindene	204.1	e	1.05	1.08	1.08	1.06
2-Ethylindene	222.5	e	1.64	1.10	1.63	1.09
3-Ethylindene	218.1	e	1.58	1.08	1.57	1.09
1,3-Dimethylindene	207.5	e	1.09	--	1.10	--
2,3-Dimethylindene	224.5	e	1.70	--	1.69	--
2,6-Dimethylindene	226.8	e	1.63	1.09	1.62	1.07
1-Methyl-3-ethylindene	64-5/1.3	e	1.62	--	1.60	--
3-Methyl-2-ethylindene	74-6/1.25	e	2.40	--	2.34	--
2,3,6-Trimethylindene	242.6	e	2.57	--	2.51	--
Benzofuran	171.38	f	0.52	0.99	0.55	1.02
Dibenzofuran	287	f	--	--	5.02	1.18

(Table III, continued)

Diphenyl ether	258.14	e	2.53	1.06	2.47	1.05
5-Methylindan	202.0	c	0.97[h]	--	0.96[h]	--
4-Methylindan	205.5	c	1.05[h]	--	1.07[h]	--
3-Methylindene	205	c	1.07[h]	--	1.09[h]	--
1,2,3,4-Tetramethylbenzene	205.04	c	1.01[h]	--	1.07[h]	--
1,6-Dimethylindan	210.9/740.0	i	1.09[h]	--	1.07[h]	--
4,7-Dimethylindan	227.6/745.5	j	1.67[h]	--	1.64[h]	--
2-Methyl-1,2,3,4-tetrahydronaphthalene	220.2	k	1.38[h]	--	1.35[h]	--
6-Methyl-1,2,3,4-tetrahydronaphthalene	229.03	c	1.75[h]	--	1.72[h]	--
1,4-Dimethylnaphthalene	268.5	c	--	--	3.70[h]	--

a Dead volume corrected.

b Defined in eq. 1.

c API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

d G. Egloff, Physical Constants of Hydrocarbons, Reinhold Publishing Corp., New York, 1957.

e Determined in this laboratory.

f From Coal Tar Research Assoc., "Coal Tar Data Book," Gomersal, near Leeds, England (1953).

g From Gesellschaft für Teerverwertung mbH, "GfT-Aromaten," Duisburg-Meiderich, Germany.

h The relative retentions of these compounds were determined from tar components identified by I. R.

i J. Entel, C. H. Ruof, and H. C. Howard, Anal. Chem. 25 (1953) 1303.

j J. Entel, Anal. Chem. 26 (1954) 612.

k A. S. Bailey and C. M. Staveley, J. Inst. Petroleum 42 (1956) 97.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF TWO AROMATIC CUTS FROM DISTILLATE FRACTIONS 10 + 11 AND 26

Peak No.	Relative retention at 220°	Compound identified by I. R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	--
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethylnaphthalene	2.93
7	3.18	2,7-Dimethylnaphthalene	3.13
		2,6-Dimethylnaphthalene	3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	1,3-Dimethylnaphthalene	3.43
		1,6-Dimethylnaphthalene	3.43

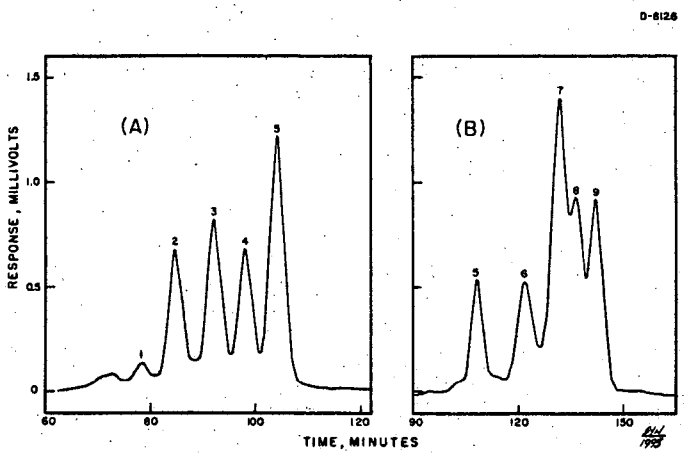

Fig. 1. Chromatograms of two aromatic cuts obtained from distillate fractions 10 + 11 (A) and 26 (B).

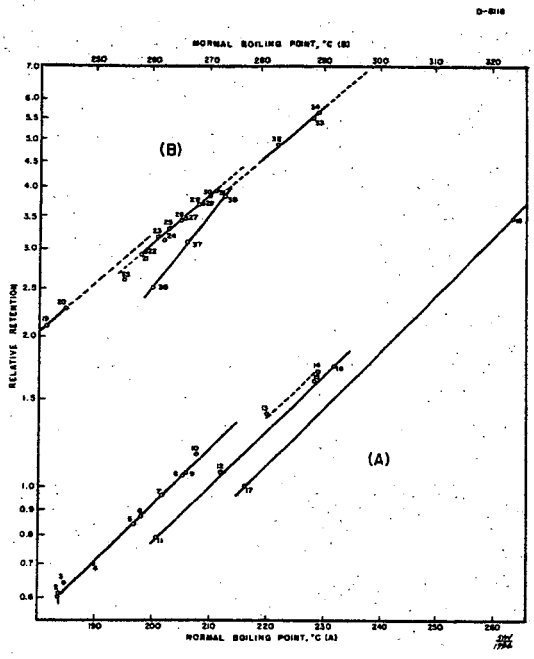

Fig. 2. Correlation between relative retentions and boiling points of some alkylbenzenes (A) and alkylnaphthalenes (B) at 220° on Apiezon L grease.

Legend:

1 1,3-Dimethyl-5-ethylbenzene
2 1,4-Diethylbenzene
3 1-Methyl-2-n-propylbenzene
4 1,2-Dimethyl-4-ethylbenzene
5 1,2,4,5-Tetramethylbenzene
6 1,2,3,5-Tetramethylbenzene
7 5-Methylindan
8 4-Methylindan
9 1,2,3,4-Tetramethylbenzene
10 1,2,3,4-Tetrahydronaphthalene
11 1-Methyl-3,5-diethylbenzene
12 1,6-Dimethylindan
13 2-Methyl-1,2,3,4-tetrahydronaphthalene
14 6-Methyl-1,2,3,4-tetrahydronaphthalene
15 4,7-Dimethylindan
16 Pentamethylbenzene
17 1,3,5-Triethylbenzene
18 Hexamethylbenzene
19 2-Methylnaphthalene
20 1-Methylnaphthalene
21 2-Ethylnaphthalene
22 1-Ethylnaphthalene
23 2,6-Dimethylnaphthalene
24 2,7-Dimethylnaphthalene
25 1,7-Dimethylnaphthalene
26 1,3-Dimethylnaphthalene
27 1,6-Dimethylnaphthalene
28 2,3-Dimethylnaphthalene
29 1,4-Dimethylnaphthalene
30 1,5-Dimethylnaphthalene
31 1,2-Dimethylnaphthalene
32 1,3,7-Trimethylnaphthalene
33 2,3,6-Trimethylnaphthalene
34 2,3,5-Trimethylnaphthalene
35 Biphenyl
36 2-Methylbiphenyl
37 4-Methylbiphenyl
38 3-Methylbiphenyl

relative retention by these curves and were used as a preliminary means of identification. Since relative retention or boiling point could not be depended on entirely for identification, confirmation of identity depended on the comparison of the infrared or ultraviolet spectra of the collected samples with published spectra of the pure compounds. However, not all of the spectra of the probable constituents could be found in the literature; to substantiate the preliminary identification, spectral-structural correlations became necessary. Table V shows eight alkylnaphthalenes identified by the second method. The details of these identifications are as follows:

(1) Constituent having a relative retention of 3.70: The boiling point of the constituent, obtained from its relative retention by the correlation curve for dimethylnaphthalenes, agreed very well with that of 1,4-dimethylnaphthalene. The identity of this naphthalene was confirmed by comparing the infrared spectrum of the constituent with that of 1,4-dimethylnaphthalene, published by the American Petroleum Institute (see Table VI).

(2) Constituents having relative retentions of 4.80 and 5.20: According to the correlation curve for trimethylnaphthalenes, the boiling points for these constituents were 281.5° and 285°, respectively. They are somewhat higher than the literature values for 1,3,6-, 1,2,6-, and 1,2,7-trimethylnaphthalene. However, the ultraviolet spectrum of the sample having a relative retention of 4.80 matched well with the literature spectrum of 1,3,6-trimethylnaphthalene. The material having a relative retention of 5.20 was found to have more than one constituent and was collected as two individual samples, one corresponding to the first half of the peak and the other the second half. By comparing the ultraviolet spectra of the two samples with the published spectra of 1,2,6- and 1,2,7-trimethylnaphthalene, the first sample was found to contain principally 1,2,6-, and the second to contain 1,2,7- as a major and 1,2,6- as a minor component.

(3) Constituents having a relative retention of 4.39: The boiling point obtained for this material from the trimethylnaphthalene correlation curve was 277.3°, a few degrees higher than any of the literature values for the four possible 1,6- and 1,7-methylethyl- and ethylmethylnaphthalenes. The identification of the material therefore depended mainly on spectral-structural correlations, as follows: An examination of the ultraviolet spectra of 1-methyl, 1-ethyl-, 2-methyl-, and 2-ethylnaphthalene showed that the two 1-alkylnaphthalenes absorb at nearly identical maxima in the region of 300 mμ to 320 mμ but differ in absorptivities; the same is true for the two 2-alkylnaphthalenes. A similar situation was also observed in the 300 mμ to 330 mμ region for 1,4,5-trimethyl- and 1,4-dimethyl-5-ethylnaphthalene and for 1,3,5-trimethyl- and 1,3-dimethyl-5-ethylnaphthalene upon examining the ultraviolet spectral data of these compounds reported by Evans, Smith, and Straus[8]. This indicates that for absorption in the 300 mμ to 330 mμ region methyl groups and ethyl groups can be interchanged without significantly changing the position of the absorption peak; however, the absorptivities are usually altered. Therefore, naphthalene substituted with one methyl group and one ethyl group could be expected to show nearly identical absorption maxima in the 300 mμ to 330 mμ region as the naphthalenes substituted with two methyl groups in the same positions. The constituents had absorption bands at 307.8 mμ, 314.7 mμ, and 322 mμ which are also exhibited by 1,6- and 1,7-dimethylnaphthalene, both of which had already been accounted for in much lower boiling fractions. It therefore appeared likely that one or more of the four possible 1,6- or 1,7-methylethyl- or ethylmethylnaphthalenes were present. The infrared spectrum of the material was in agreement with this conclusion. According to Werner, Kennard, and Rayson[9], the two strong bands shown in the sample spectrum at 783 $cm.^{-1}$ and 810 $cm.^{-1}$ could be due to 3H and 2H out-of-plane deformation vibrations of 1,6-disubstituted naphthalene, and the other two strong bands at 760 $cm.^{-1}$ and 835 $cm.^{-1}$ could be due to the same vibrations of 1,7-disubstituted naphthalene.

TABLE V

IDENTIFICATION OF EIGHT ALKYLNAPHTHALENES

Relative retention at 220°	Compound	Literature[a] b.p., °C. 760 mm.	B.p., °C. obtained from the correlation curve	Spectroscopic identification
3.70	1,4-Dimethylnaphthalene	268.5	268.4	Infrared
4.80	1,3,6-Trimethylnaphthalene	280	281.5	Ultraviolet
5.20	1,2,6-Trimethylnaphthalene	280	285	Ultraviolet
	1,2,7-Trimethylnaphthalene	278		Ultraviolet
4.39	1-Methyl-6-ethylnaphthalene, or 1-Ethyl-6-methylnaphthalene	273 / 270	277.3	Ultraviolet and infrared spectral-structural correlations
	1-Methyl-7-ethylnaphthalene, or 1-Ethyl-7-methylnaphthalene	271 / 270		
4.15	2-Methyl-6-ethylnaphthalene	270	275.2	Ultraviolet and infrared spectral-structural correlations
	2-Methyl-7-ethylnaphthalene	270		

a API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

TABLE VI

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight, g.	Wt. % in neutral oil[a]
1,2,3,4-Tetramethylbenzene[b]	6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.0681	0.153
1,2-Dimethyl-3-n-propylbenzene[b]	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.2976	0.042
1,4-Dimethyl-2-n-propylbenzene[b]	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.5874	0.084
1-Methyl-2,4-diethylbenzene[b]	6-13	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.9873	0.141
5-Methylindan[b]	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7566	0.251
4-Methylindan[b,d]	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7389	0.249
1,6-Dimethylindan	7-14	Rel. retention-b.p. correlation, I.R.	c	2.3746	0.340
4,7-Dimethylindan	7-16	Rel. retention-b.p. correlation, I.R.	c	1.3034	0.186
3-Methylindene[b]	5,6,7,8	I.R.	c	0.7141	0.102
3-Ethylindene	7-17	Rel. retention, I.R.	e	1.3126	0.188
2-Ethylindene	7-17	Rel. retention, I.R.	e	1.3032	0.186
2,3-Dimethylindene	7-17	Rel. retention, I.R.	e	1.7762	0.254
1,2,3,4-Tetrahydronaphthalene[b,d]	5,6,7,8	Rel. retention, I.R.	e	0.6170	0.088

(Table VI, continued)

2-Methyl-1,2,3,4-tetrahydro-naphthalene	7-15	I.R.	c	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydro-naphthalene	12,13,14,15	I.R.	c	0.4958	0.071
Naphthalene[b,d]	6-15	Rel. retention, I.R.	e	6.3853	0.914
1-Methylnaphthalene[d]	14-24	Rel. retention, I.R.	e	12.0615	1.728
2-Methylnaphthalene[d]	12-24	Rel. retention, I.R.	e	16.1630	2.315
1-Ethylnaphthalene	20-29, 1*[f]	Rel. retention, I.R.	e	1.9777	0.283
2-Ethylnaphthalene	20-29, 1*	Rel. retention, I.R.	e	3.1184	0.456
2,7-Dimethylnaphthalene	21-29, 1*,2*	Rel. retention, I.R.	e	4.8187	0.690
1,7-Dimethylnaphthalene	23-29,1*,2*	Rel. retention, I.R.	e	4.7915	0.686
2,6-Dimethylnaphthalene[d]	23-29,1*,2*	Rel. retention, I.R.	e	4.1664	0.596
1,6-Dimethylnaphthalene[d]	25-29,1*-5*	Rel. retention, I.R.	e	6.4648	0.926
1,3-Dimethylnaphthalene	25-29,1*-5*	Rel. retention, I.R.	e	6.5617	0.940
2,3-Dimethylnaphthalene[d]	27,28,29, 1*-7*	Rel. retention, I.R.	e	3.8247	0.547
1,5-Dimethylnaphthalene	28,29,1*-7*	Rel. retention, I.R.	e	3.6861	0.528
1,2-Dimethylnaphthalene	29, 1*-7*	Rel. retention, I.R.	e	3.5632	0.510
1,4-Dimethylnaphthalene	3*,4*	Rel. retention-b.p. correlation, I.R.	c	0.0979	0.014
2-Methyl-6-ethylnaphthalene 2-Methyl-7-ethylnaphthalene	4*-8*	Rel. retention-b.p. correlation, U.V. and I.R. structural correlations	-	3.9029	0.559
1-Methyl-7-ethylnaphthalene[g] and/or 1-Methyl-6-ethylnaphthalene[g]	4*-8*	Rel. retention-b.p. correlation, U.V. and I.R. structural correlations	-	3.2925	0.471
1,3,6-Trimethylnaphthalene	5*-7*	Rel. retention-b.p. correlation, U.V.	h	0.7338	0.105
1,3,7-Trimethylnaphthalene	5*-7*	Rel. retention, I.R.	e	0.452	0.064

(Table VI, continued)

1,2,6-Trimethylnaphthalene 1,2,7-Trimethylnaphthalene	6*-8*	Rel. retention-b.p. correlation, U.V.	h h	0.8751	---
Biphenyl[d]	18-29,1*	Rel. retention, I.R.	e	18.8235	2.696
4-Methylbiphenyl	28,29,1*,2*	Rel. retention, I.R.	e	0.7271	0.104
3-Methylbiphenyl	1*-7*	Rel. retention, I.R.	e	1.2431	0.178
Cyclohexyl benzene	12-15	Rel. retention, I.R.	e	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene	20-26	Rel. retention, I.R.	e	1.1713	0.167
Acenaphthylene	4*-6*	Rel. retention, I.R.	e	0.6963	0.099
Acenaphthene[d]	2*-8*	Rel. retention, I.R.	e	2.336	---
Diphenyl ether	18-29,1*,2*	Rel. retention, I.R.	e	38.5897	5.528
2,3-Dimethylbenzofuran	14-16	I.R.-structural correlation	-	0.1778	0.025
Dimethylbenzofuran II	7-13	I.R.-structural correlation	-	1.7848	0.255
Dimethylbenzofuran III	9-15	I.R.-structural correlation	-	0.6451	0.092
Dibenzofuran	5*-8*	Rel. retention, I.R.	e	1.4718	---

a Total neutral oil distilling up to about 360°, representing 16.92 wt. % of the total tar.

b Identified in prior work by this laboratory[1].

c American Petroleum Institute, Research Project 44, Infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

d Previously identified by others[2-6].

e This laboratory.

f Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report[1].

g The positions of the ethyl and methyl groups might be reversed.

h E. Heilbronner, U. Fröhlicher and P. A. Plattner, Helv. Chim. Acta, 32 (1949) 2479.

(4) Constituents having a relative retention of 4.15: This material appeared to consist of a mixture of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. The boiling point of the sample found by the trimethylnaphthalene curve was several degrees higher than the literature value for the two naphthalenes. However, the ultraviolet absorption maxima in the 300-330 mμ range for the constituent producing the first half of the peak were at 303 mμ, 310 mμ, 317 mμ, and 324.8 mμ, in close agreement with the much lower boiling 2,6-dimethylnaphthalene. The maxima shown by the second constituent were nearly identical to those for 2,7-dimethylnaphthalene at 307 mμ, 317 mμ, and 321 mμ. The presence of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene was thus indicated. The infrared bands at 800 $cm.^{-1}$ to 900 $cm.^{-1}$ substantiated these identifications. The strong bands shown by the first constituent at 823 $cm.^{-1}$ and 874 $cm.^{-1}$ and those shown by the second constituent at 835 $cm.^{-1}$ and 876 $cm.^{-1}$ could be due, respectively, to 2H and 1H out-of-plane deformation vibrations of 2,6- and 2,7-disubstituted naphthalenes[9].

In addition to these alkylnaphthalenes, three dialkylbenzofurans, of which one might be the 2,3-dimethyl-isomer, were tentatively identified by the characteristic infrared bands of benzofurans, observed by examining the spectra of benzofuran and all its monomethyl derivatives[10]. A strong band between 1,250 $cm.^{-1}$ and 1,280 $cm.^{-1}$ and one or two between 1,090 $cm.^{-1}$ and 1,160 $cm.^{-1}$ could be characteristic of benzofurans. According to Bellamy[11], compounds containing the structure = C - O - may absorb near 1,250 $cm.^{-1}$ and in unsaturated cyclic compounds, with the structure = C - O - C = , a band may appear near 1,100 $cm.^{-1}$ or somewhat higher frequencies. Therefore, in the spectra of the benzofuran constituents, the bands between 1,250 $cm.^{-1}$ and 1,280 $cm.^{-1}$ and between 1,090 $cm.^{-1}$ and 1,160 $cm.^{-1}$ may be due to the furan structure in the molecule.

One benzofuran sample, having a relative retention of 1.28 at 200°, showed a strong band at 1,251 $cm.^{-1}$ as in 2-methylbenzofuran and another strong band at 1,092 $cm.^{-1}$ as in 3-methylbenzofuran. This sample also absorbed strongly at 742 $cm.^{-1}$, similarly to 2-methyl- and 3-methylbenzofuran, both of which have a band at 746 $cm.^{-1}$ that is probably due to the 4H out-of-plane deformation vibration in the benzene ring. The boiling point of 2,3-dimethylbenzofuran from the literature[12] is approximately 220°, which falls in the boiling range of the distillate fractions containing this component. It is, therefore, very likely that this constituent is 2,3-dimethylbenzofuran. The other two samples showed the characteristic infrared bands of benzofurans in both regions. In addition, a few sharp bands also appeared between 1,000 $cm.^{-1}$ and 1,400 $cm.^{-1}$. These were considered to be dimethylbenzofurans, all of the isomers of which boil well within the range 210° to 230°.

Quantitative estimation of aromatic hydrocarbons

The internal standard method, which was described in the previous paper[1], was employed for quantitative analysis of the samples, 1,2,3-triethylbenzene being selected as the standard. The equation used for the calculations is as follows:

$$f_C = A_s W_c / A_c W_s \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where f_C is the calibration factor, as defined, A_s and A_c are the areas for the standard and component in the mixture, and W_c and W_s are the weight-percentages of the compound and the standard. The f_C values for a number of aromatic hydrocarbons were determined at 200° and 220° and are given in Table III. No significant difference was found between the values for each compound at these two temperatures. These values were used to determine the weight-percentages of the constituents in the fractions. For those compounds present in the tar for which authentic specimens were not available, the f_C values of their isomers or of structurally similar compounds were used. For example, an average f_C of 1.03 for six dimethylnaphthalenes was used to calculate the amounts of the 1,2- and 1,4-dimethyl isomers, an average of 1.08 for three trimethylnaphthalenes was used for other trimethyl and

methylethylnaphthalenes, the f_C value of 0.99 for 1,2,3,5-tetramethylbenzene was used for 1,2,3,4-tetramethylbenzene, the value of 1.42 for indan was used for all indan derivatives, the value of 1.52 for tetralin was used for the two methyltetralins, and 1.05, an average of the values for 2-methyl- and 3-methylbiphenyl, was used for 4-methylbiphenyl.

The aromatic hydrocarbons boiling between 202° and 280° found in the low-temperature bituminous tar and their quantities are presented in Table VI. The values of weight-percentages in neutral oil of the three highest boiling components are not entered, since they are also expected to be present in the next higher boiling fraction.

DISCUSSION

Correlation between relative retentions and boiling points of alkylbenzenes and alkylnaphthalenes

When the logarithms of relative retentions at 220° for alkylbenzenes and for alkylnaphthalenes, in either instance having an equal number of carbon atoms in the alkyl groups, were plotted against their boiling points, a straight line resulted. The relationship is similar to that established for a number of alkylbenzenes at 150°, as previously reported[1].

Figure 2 (A) shows three parallel lines corresponding to alkylbenzenes having 4, 5, and 6 carbon atoms in the alkyl groups. Indans, which have a benzene nucleus with a 1,2-trimethylene-type alkylation, fall closely on the correlation curves for alkylbenzenes having the corresponding number of carbon atoms in alkyl groups. However, tetralin (point 10 in Fig. 2), which has a 1,2-tetramethylene-type alkylation, does not fit so closely to the line for C_{10}-alkylbenzenes, and its 2-methyl- and 6-methyl-derivatives (points 13 and 14) are well off the line for C_{11}-alkylbenzenes. However, a line drawn between points 13 and 14 is essentially parallel to the line for the C_{11}-alkylbenzenes. No clear-cut relationship can be established between the indans and the tetralins with this limited data for alkyltetralins.

Figure 2 (B) shows three parallel straight lines corresponding to alkylnaphthalenes having 1, 2, and 3 carbon atoms in the alkyl groups. A fourth line representing three monomethylbiphenyls (points 36, 37, and 38) is not parallel to the naphthalene lines.

A difference in slope can be observed among the three groups—benzenes, naphthalenes, and biphenyls. The slope of the benzenes is 0.0113, that of the naphthalenes is 0.0098, and that of the biphenyls is 0.0164.

ACKNOWLEDGMENTS

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FIA ANALYSIS OF COAL TAR

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Several rapid and simple analytical procedures have been used for coal tar assay; likewise, many long and tedious methods have been worked out. The rapid, simple methods are generally criticized for not giving sufficient information while the long, tedious methods are unpopular because they are just that--long and tedious. The present system is offered as an analytical tool which is neither very tedious nor greatly time consuming but which gives considerable useful information.

The Fluorescent Indicator Adsorption (FIA) method was originally designed for use on light petroleum fractions of a fluid nature. Essentially it consists of displacement adsorption chromatography of hydrocarbon mixtures on a silica gel column, fluorescent indicators being used to detect the zones containing the various chemical types, namely, saturates, olefins, and aromatics.

Adaptation of FIA to Coal Tar

Two major problems were encountered by the Bureau of Mines in adapting this analysis for use on coal tar. First, the tar is often too viscous to flow in a chromatographic column, and second, coal tar contains compounds other than hydrocarbons such as neutral oxygenates, tar acids, and tar bases.

First attempts by the Bureau to chromatograph samples of low-temperature tar were unsuccessful, as the waxes would solidfy during fractionation and prevent the movement of the sample in the column. A steam-heated column was constructed, but the silica gel would not absorb at the elevated temperature, and no separation was possible. Attempts were made to remove the waxes by precipitating them from a cold acetone solution of the tar or by extracting them with petroleum ether. Neither system was satisfactory, as it was difficult to establish with any accuracy just how much wax was removed. The problem was finally solved by diluting the tar with a precisely measured amount of petroleum ether; this served to dissolve the waxes and allowed the tar to move freely down the column, and since the amount of petroleum ether added was known, this could be corrected for in the results.

For solution of the second problem, it was necessary to demonstrate that the FIA method could be used to separate nonhydrocarbon materials as well as hydrocarbons, because the nonhydrocarbons make up a large part of the tar. A synthetic mixture, composed of heptane, octene, benzene, acetophenone, and o-cresol, was made up for this demonstration. When this mixture was run using the standard FIA dyed-gel, the hydrocarbons separated in the usual manner; the acetophenone section then took up the pink dye which normally indicates the end of the chromatogram; the cresol section, a light tan color, followed.

Gross tar, distilled to its cracking temperature, separated on the silica gel column into the same number of zones, but the dark color of the neutral-oxygen and tar acid fractions made it impossible to detect visually the boundary between these two zones. When samples from these sections were examined by infrared spectra, however, bands characteristic of ketone and phenolic hydroxy groups were identified.

Attempts to determine tar bases by the FIA method have so far been unsuccessful.

At this stage of development, it became apparent that not all of the tar sample was being eluted. To correct this failure, changes were made in column design, and stronger displacing agents were employed. Eventually a satisfactory charging column was evolved, and pyridine was chosen as the most suitable displacing agent.

It was found that definition of the boundaries between the various groups was far better when gravity flow was used than when the separation was carried out under pressure. The charging column, therefore, was designed to facilitate the flow so that an analysis by this technique could be completed in a reasonable time. By shortening the charging sections and eliminating the usual capillary, highly satisfactory separations were realized in 6 to 8 hours.

Best results have been obtained from distilled tars. Gross, undistilled tar contains polymeric material and heavy pitch which often obscure the top level of the chromatogram. Tar fractions and whole tars distilled to any temperature up to the cracking point give excellent results. If distillation is impractical or undesirable, the tar can be separated from most of the pitch by dissolving in ether and filtering, or the sample can be washed through a silica gel column with low-boiling petroleum ether or heptane until the eluent is clear, then stripped of solvent.

This, then, is the assay system in its current stage of development. The charging tube consists of two sections, each 10 cm. long; the upper section is 12 mm. OD while the lower is 7 mm. OD. These tubes are joined in a smooth taper, and the lower end of the lower section is tapered to fit into 1/8-inch Tygon tubing that is used to attach the measuring tube. The measuring tube is 3 mm. OD and 120 cm. long and is drawn out to a capillary on the lower end. Davison 923 silica gel, which has been activated at 200° C. overnight, is then funneled into the column. Packing the column is most easily done by attaching a vibrator to a ring stand and clamping the column to this stand. The vibrator is run throughout the packing operation, both to aid filling and to insure uniform packing. When the column has filled to the middle of the 7-mm. section, a small amount of dyed gel is added, and then plain silica gel again to bring the level to about the middle of the upper section.

The sample is prepared by placing 2 ml. of petroleum ether into a 10-ml. graduate and adding tar to bring the level of the mixture to the 4 ml. mark. One to two ml. of pyridine are added and the sample is then well mixed. One ml. of this sample mixture is placed directly on the silica gel in the column, and as soon as the sample is completely adsorbed, an additional layer of 2 to 3 cm. of silica gel is placed on top of the column and packed down. Eluent is added and the chromatogram allowed to develop by gravity flow.

When the upper boundary of the sample is well into the measuring tube, the column is placed in a dark room, where it is illuminated with ultraviolet light and the various sections measured with a meter stick. Half of the total length is due to the added petroleum ether and therefore is subtracted from the length of the saturate section. What remains in this section represents the saturates from the tar. The remaining sections are measured, and the length of each section is proportional to the amount of that chemical type present in the tar.

Results from FIA Assay System

Sine this method is not fully developed, it has not been used extensively on specific assay problems; however, in the course of development, some interesting facts have been disclosed. Confirmation of considerable amounts of oxygen-containing material in the neutral oil is of interest. The FIA analysis of a typical neutral oil fraction from lignite tar follows:

FIA ANALYSIS OF A NEUTRAL OIL FRACTION

Boiling 301-304° C.

Saturates, vol. per cent	18.4
Olefins	7.1
Aromatics	53.3
Oxy-compounds	21.2

The maximum oxygen content of this neutral oil is 3 per cent; therefore, it would seem unreasonable to find that 21 per cent of the sample is oxygen-containing compounds. The mean molecular weight, however, is in the order of 200, and if each such molecule contained a single oxygen atom, the oxygen content would be 8 per cent. To bring the oxygen content to 3 per cent, 350-gram atoms of oxygen-free material must be assumed, for a total of 550-gram atoms. Of this, 36-weight per cent is oxygen-containing material. From this we can see that 21 per cent oxygen-containing neutral compounds in a sample containing 3 per cent oxygen is not at all unreasonable.

Several assays, including cuts from various temperature ranges as well as those distilled over the full boiling range, have been made on distilled fractions of gross tar. Further refinements are necessary before the method can be fully evaluated for this purpose, but there is little doubt that the FIA analysis can be used to differentiate between various tars and to give a good estimate of the chemical types they contain. As an example, the comparative analyses of tars obtained from a North Dakota and a Texas lignite follow.

FIA ASSAY OF TWO GROSS TARS

(Boiling 80-360°)

	North Dakota Tar	Texas Tar
Saturate, vol. per cent	15.1	16.7
Olefins	7.6	10.1
Aromatics	29.7	34.9
Oxy-compounds (neutral + acid)	48.4	38.4

Future Problems

Foremost among the remaining problems is that of distinguishing the boundary between neutral oxy-compounds and tar acids. The boundary is easily observed in very light-colored samples but is completely obscured in the dark color of most tars.

Another desirable development would be a more rapid analysis, particularly for control work. Any speedup would almost certainly result in loss of accuracy, although this loss could be minimized to a tolerable level in most cases. At present, the average run takes about 6 hours.

Eventually, if the system is to be completely general, means must be found to determine tar bases.

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APPLICATION OF HIGH VACUUM MICRO-DISTILLATION TO THE STUDY OF COAL-TAR AND PETROLEUM PITCHES

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INTRODUCTION

The binder pitches used in the manufacture of carbon electrodes are of coal-tar or petroleum origin and exhibit pronounced differences in their properties depending on their source and mode of production. Various means have been devised to detect these differences, but distillation has very seldom been used. Obviously there are many reasons for this lack of interest in distillation, but the main one is probably the thermal lability of this type of material or at least of some of its constituents. However, the difficulty associated with the thermal lability can be overcome by making use of high vacuum technique.

There are a number of molecular stills commercially available, but, in general they require the use of fairly large samples. In the investigation described herein this was a major handicap since the available samples were mostly experimental and of limited supply. Furthermore, we were not interested in collecting fractions and studying each fraction as the amount of work involved would have been prohibitive, especially in view of the fact that it was intended to test a fairly large number of samples; past experience in our own laboratory had clearly indicated that work based on only a few samples cannot be really informative as the conclusions drawn can be greatly influenced by the type of pitch used and the treatment the pitch has undergone. Our main interest was to find out whether distillation could yield significantly different data which might be useful in pitch evaluation. The micro-molecular still used by Sims[1] for the analytical distillation of organic mixtures appeared to offer the desired features; the technique was reasonably rapid and requires only milligram quantities of material. With such a still the amount of distillate at various temperatures is calculated from the measured contraction of a calibrated quartz helix.

EXPERIMENTAL

Still. - The apparatus (Figure 1) consists essentially of a pan suspended from a quartz helix in an evacuated Pyrex tube. The sample is heated by an internal heating coil and the contraction of the quartz helix due to the loss of weight of the sample in the course of distillation is measured by a sensitive-reading cathetometer.

The sample pan is made of aluminium. A disk of 5/8 in. diameter is stamped out of a sheet of aluminium foil by using a steel punch, and formed into a cylindrical pan of 3/8 in. diameter and 1/8 in. high wall in a specially designed mould. The aluminium pan has an area of 0.75 cm^2 and weighs approximately 10 mg.

The stirrup, which holds the pan, is cut from a sheet of stainless steel of approximately 0.0065 in. thickness. It is in the shape of a cross with arms 1 1/2 mm wide; the length of the 3 short arms is 6 mm, the length of the long arm, 33 mm. The ends of the arms are bent upwards in such a way that the pan can be placed between them. The end of the long arm is shaped into a hook to be inserted into the loop of the Pyrex filament which in turn is hung on the quartz helix (Figure 1). The weight of the stirrup is reduced to approximately 50 mg by immersion in hydrochloric acid.

The heating coil, 6 in. long and 1/2 in. in diameter, has a resistance of 14 ohms. It is made of 24 gauge Chromel "A" wire and is wound on three strip-mica spacers. The voltage is controlled by a variable transformer (Variac), with a range of 0-135 volts and a maximum output current of 7.5 amperes. The maximum temperature of 350°C inside the heating coil is obtained by operating at a Variac setting of 60 (60 volts).

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Since the pan containing the sample is continuously moving upwards during a distillation, due to the loss of weight, it was important to know the temperature distribution inside the heating coil. The temperature, after the still had been evacuated, was raised to 350° C at a rate of approximately 6.6° C per minute by increasing the Variac by one scale division every minute; the temperature was measured by means of the chromel-alumel thermocouple on the central axis of the heating coil. The thermocouple was moved in steps of 1/2 in. and at each position the heating cycle was repeated and temperatures were recorded. The position of the thermocouple was measured by means of a scale printed on the wall of the still proper; the zero of the scale was level with the top of the heating coil. Figure 2 shows the axial temperature distribution of the heating coil.

The heating rate of approximately 6.6° C/minute was initially selected because of practical considerations. A higher heating rate was not desirable since gas evolution during distillation would be too fast. A slower heating rate (Variac setting increased by one scale division every second minute, which meant double distillation time) was tried, but did not change the results significantly; the shape of the elimination curve stayed the same except that the peak of the curve moved slightly towards a lower temperature.

By raising the Variac by one scale division every minute, the temperature, however, did not increase at a satisfactorily uniform rate; the heating rate was slightly higher at the beginning than at the end of distillation. A modified scale was prepared for the Variac and it was then possible to obtain a heating rate of 6.6° C/minute throughout the distillation.

Vacuum System. - The system was evacuated by a Duo-seal, two-stage vacuum pump. (Canadian Laboratory Supplies Limited, Catalogue No. A-72-703B). High vacuum was obtained by a Supervac OD-25 Oil Diffusion Pump, (Central Scientific Company, Catalogue No. 93330, No. 1), and was measured by a McLeod gauge. Apiezon grease "N" was used for all glass joints and stopcocks.

Measuring Device. - The relative position of the pan - and thus the weight loss of the sample during a distillation - was measured by a Wild cathetometer (H. Wild, Surveying Instruments Supply Company, Ltd., Heerbrugg, Switzerland). The cathetometer consists of a horizontal telescope with a magnification of 12x, mounted so as to slide upon an upright pillar with an attached glass staff. The telescope is adjusted in height by rack and pinion action until its corsshairs coincide with the lowest end of the quartz helix. The position of the telescope upon the vertical, graduated glass staff can then be read by means of a microscope. Direct reading to 0.1 mm and safe estimation to 0.01 mm can be made with this instrument.

Calibration of Quartz Helix. - Analytical balance weights, covering a range up to 100 mg, were placed in the sample pan and the extension of the quartz helix caused by each weight increase measured with the cathetometer. For each one milligram increment in load, the helix was lengthened by 1.1092 mm.

Contraction of the quartz helix in the course of a distillation was due to two causes: (a) reduction in load as a result of distillation and (b) heating of the quartz helix. The thermal contraction of the helix was measured over the entire temperature range from room temperature to 350° C; it was found to be roughly 0.01 mm per 6.6° C within the normal distance travelled by the pan during a distillation. Positive corrections were accordingly made to all cathetometer readings.

Sample Preparation. - Preliminary distillations had shown that at a temperature between 80 and 150° C, bubbles due to gas evolution started to form on the surface of the pitch. The bubbles gradually increased in size and finally collapsed, imparting a jerking motion to the pan so that it was impossible to take readings on the cathetometer. It was finally found that with a mixture of 30% pitch and 70% calcined petroleum coke no bubbling occurred and the readings on the cathetometer could be made without difficulty. A blank distillation run with coke alone showed that no trace of volatile was present in the coke.

Coke, calcined at 1400° C and ground to -35 +48 mesh, was mixed in a mortar with finely ground pitch (-20 mesh) in the ratio of 2:1. From this mixture, 166.5 mg (55.5 mg pitch) were weighed into the aluminium pan. This particular sample size was chosen because (a) the cathetometer readings could be multiplied directly by the factor 2 in order to obtain the percentage distilled, and (b) the pan remained within a zone of reasonably uniform temperature throughout the complete distillation cycle, as shown in Figure 2.

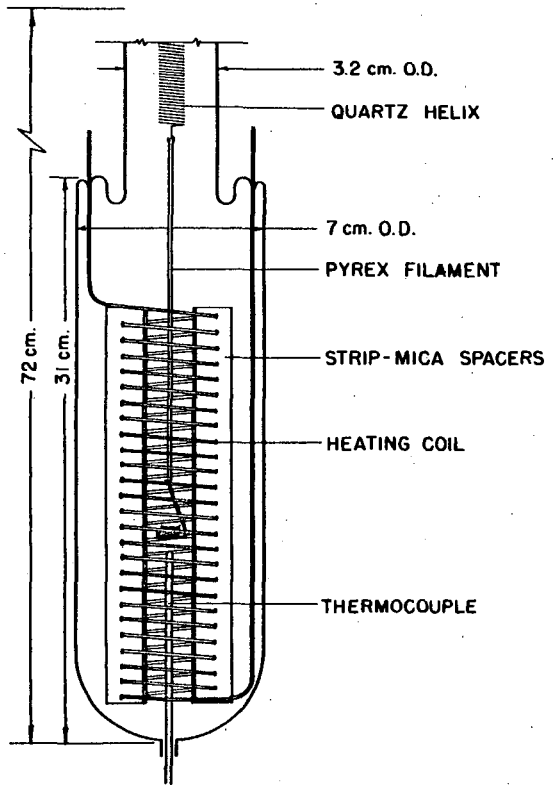

FIGURE 1

MICRO POT-TYPE STILL

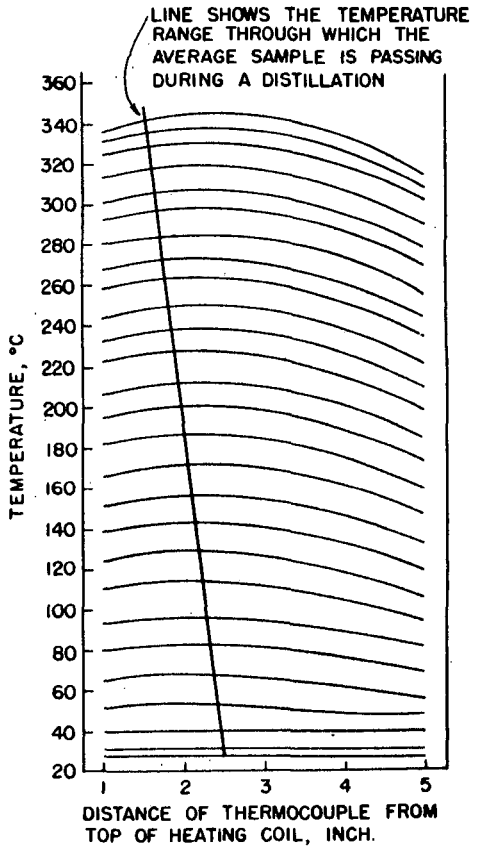

FIGURE 2

AXIAL TEMPERATURE DISTRIBUTION OF HEATING COIL.

Distillation Procedure. - After the pressure of the system has been reduced to 10^{-5} mm Hg as read on the McLeod gauge, the sample was gradually heated up to 350° C. In the course of the distillation, the contraction of the helix was recorded at constant intervals of one minute. To prevent condensation on the still wall facing the cathetometer and thus interference with the telescope readings, a jet of air was played on the appropriate area of the wall.

RESULTS

A series of 20 binders - 17 coal-tar pitches and 3 petroleum pitches - was tested. They are identified in Table 1 which also lists their respective melting point, coking value, atomic carbon-hydrogen ratio, and compressive strength of test electrodes prepared from a mixture of petroleum coke and binder pitch; this last property is considered as the best individual criterion of binder quality.

Distillation runs yielded more than 1000 readings, which it is impractical to reproduce. The data were plotted in two fashions, as elimination curves and as distillation curves. Elimination curves represent the amount of distillate in each fraction expressed as weight percentage of the initial sample weight, while distillation curves relate temperatures to cumulative distillate percentages.

For present purposes, a selection has been made of three pitches - two coal-tar and one petroleum pitches - that illustrate the general behaviour pattern and also the more or less extreme ranges encountered. Figure 3, shows elimination curves, Figure 4, cumulative distillation curves for the same three pitches.

TABLE 1

DESCRIPTION OF PITCH SAMPLES

Pitch Identification[a]	Melting Point[b] °C	Coking Value[c] %	Carbon-Hydrogen Ratio (Atomic)	Compressive Strength of Test Electrodes (kg/cm^2)
		Coal-Tar Pitches		
A-1	137	64.8	1.86	444
A-2	145	69.5	1.88	440
A-3	101	57.9	1.79	354
A-4	106	57.8	1.75	352
A-5	67	51.1	1.77	340
A-6	97	55.6	1.76	336
A-7	68	45.0	1.64	289
A-8	66	41.5	1.61	273
B-1	89	54.4	1.67	381
B-2	94	58.5	1.84	348
B-3	89	56.6	1.83	341
B-4	95	56.9	1.76	339
B-5	90	51.7	1.76	320
B-6	89	51.4	1.71	305
B-7	89	53.5	1.59	295
B-8	95	49.5	1.62	252
C-1	65	32.9	1.49	181
		Petroleum Pitches		
D-1	111	53.3	0.98	210
D-2	111	43.1	0.93	169
E-1	70	42.9	1.12	135

(a) A, B, C, D, E indicate different suppliers.
(b) Cube-in-air method was used for melting points greater than 80° C; below 80° C, cube-in-water.
(c) Method described in literature reference (2).

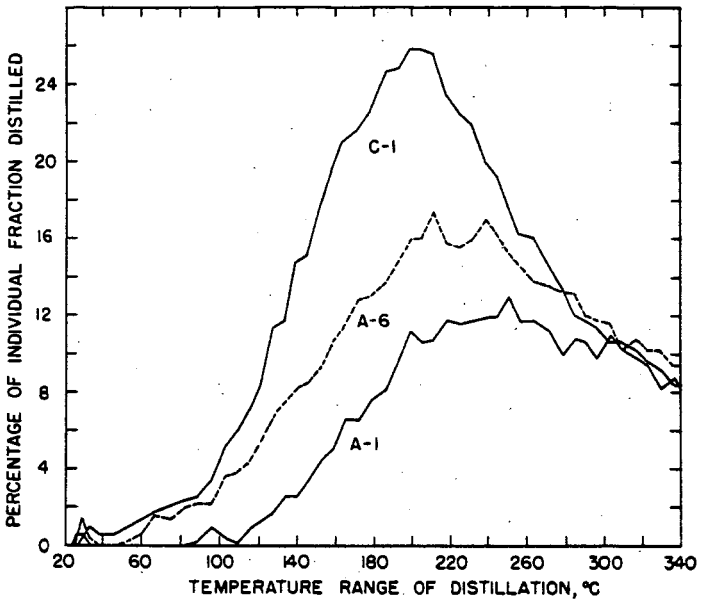

FIGURE 3

ELIMINATION CURVES OF PITCH SAMPLES

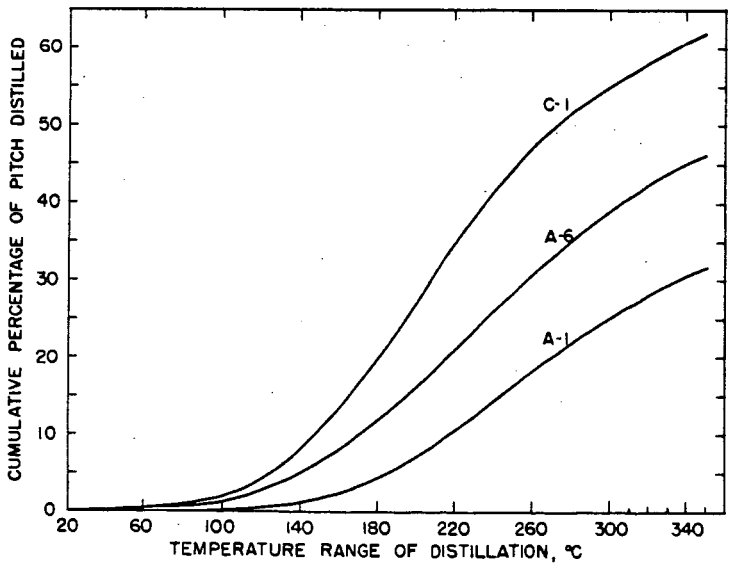

FIGURE 4

CUMULATIVE DISTILLATION CURVES OF PITCH SAMPLES

DISCUSSION

From examination of the various curves, the three variables which appeared to be of some significance for pitch characterization were estimated to be (a) the slope of the relatively straight portion of the cumulative distillation curve, (b) the temperature at which the greatest percentage was distilled (elimination maximum) and (c) the cumulative percentage corresponding to the elimination maximum.

In general these three variables could have been obtained from the distillation curves, but in some cases the precision was inadequate. This difficulty was overcome by establishing the mathematical equation of each cumulative distillation curve and subsequently deriving the values shown in Table 2. As can be observed in Figure 4, the shape of the cumulative distillation curves is that of an elongated S; the "Gompertz" equation[3] was found to be satisfactory in defining such curves:

$$y = a.b^{c^x} \qquad \text{or}$$

$$\log y = \log a + c^x \log b$$

Inspection of Table 2 shows that low values of maximum slope (x_1) and amount distilled at the elimination maximum (x_2) tend to coincide with high values of compressive strength; this indicates some measure of individual relationships. Such a tendency does not exist for the elimination maximum (x_3). Inspection alone, however, is inadequate to give a full appraisal of relationships and a better picture is supplied by statistical study.

The statistical procedure applied was the Multiple Correlation Technique[4] designed to assess the relationship between two or more variates. Complete statistical data are not reported herein; only those useful for the discussion of results are summarized in Table 3.

Statistically speaking the correlation coefficients given in Table 3 for maximum slope ($R = 0.903$) and for % distilled ($R = 0.766$) are highly significant but, from a practical viewpoint, the standard deviations about regression of compressive strength on either one of the two independent variables ($\sigma = 36.7$ and 54.7 kg/cm^2 respectively) are rather high. In other words, although the maximum slope alone accounts for 81.4% (R^2) of the variations in compressive strength, and % distilled alone, for 58.7%, the proportion of variations in compressive strength not accounted for is undesirably high. It was thought then that, taken together, variations in slope and % distilled, or even variations in all three independent variables might account for a much higher proportion of the variations in compressive strength. However, tests 3, 4 and 5 of Table 3 clearly indicate that this was not the case. In fact the correlation between compressive strength and slope alone (test 1) is as good as the correlation between compressive strength and any combinations of two or three independent variables.

From the above discussion, it can be concluded that high vacuum micro-distillation of pitch, as carried out during this investigation, represents another analytical tool which permits a certain differentiation between various pitches, but this differentiation is not considered satisfactory for prediction of pitch quality. However, it is believed that, because of its good reproducibility, it could be used advantageously as another means of controlling pitch uniformity.

ACKNOWLEDGEMENTS

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TABLE 2

MAXIMUM SLOPE, PERCENTAGE DISTILLED AT ELIMINATION MAXIMUM AND ELIMINATION MAXIMUM OF PITCH SAMPLES
(in order of decreasing compressive strength of test electrodes)

Pitch Identification	Compressive Strength kg/cm^2	Maximum Slope (x_1) %/°C	Amount Distilled (x_2) %	Elimination Maximum (x_3) °C
		Coal-Tar Pitches		
A-1	444	.1848	15.2	243
A-2	440	.1824	15.4	259
B-1	381	.1998	19.4	191
A-3	354	.1993	19.2	207
A-4	352	.2170	20.4	235
B-2	348	.2192	20.8	220
B-3	341	.2348	20.6	217
A-5	340	.2626	21.4	192
B-4	339	.2294	24.8	236
A-6	336	.2421	21.2	218
B-5	320	.2035	21.5	216
B-6	305	.2270	23.2	225
B-7	295	.2486	22.4	217
A-7	289	.2956	22.8	182
A-8	273	.3135	26.0	199
B-8	252	.2269	20.0	200
C-1	181	.3706	25.8	194
		Petroleum Pitches		
D-1	210	.3116	22.3	286
D-2	169	.3470	24.8	289
E-1	135	.3698	23.9	251

TABLE 3

CORRELATION BETWEEN COMPRESSIVE STRENGTH AND DISTILLATION DATA

Test No.	Variables[a]	Correlation Data[b] R	R^2	Standard Deviation[c] (kg/cm^2)
1	x_1	0.903	0.814	36.7
2	x_2	0.766	0.587	54.7
3	x_1, x_2	0.910	0.828	36.4
4	x_1, x_3	0.905	0.819	37.3
5	x_1, x_2, x_3	0.916	0.838	36.3

(a) x_1 = maximum slope; x_2 = % distilled at elimination maximum; x_3 = elimination maximum.

(b) R_2 = correlation coefficient
R x 100 = % of total variation in compressive strength accounted for by the variations in the specified independent variables or combinations of them.

(c) Standard deviation about regression of compressive strength on the independent variables or combinations of them.

SOLVENT FRACTIONATION OF ELECTRODE BINDER PITCHES

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INTRODUCTION

Solvent fractionation has been used fairly extensively for studying composition and structure of pitches. Among the more recent papers published on the subject are those of Wood and Phillips,[1] Mallison,[2] Franck,[3] and Lissner and Schäfer.[4] However, most of the studies dealt with a small number of samples and rather elaborate fractionation techniques. Past experience in our own laboratory has indicated that there is danger in studying too few samples: the conclusions drawn can be greatly influenced by the types of pitch used or by the treatment the pitch has undergone. For these considerations, and also because the time involved even for simple fractionation is always fairly long, it was preferred to try a fractionation procedure which would be relatively simple in operation as well as in number of fractions produced, thus allowing the coverage of a large number of binders. A two-stage fractionation, which would permit isolation of the much-discussed carbon-I (C-I), appeared appropriate.

EXPERIMENTAL

Choice of Solvents

In order to select the most suitable fractionation agents, 14 solvents were examined. The procedure employed consisted in refluxing 1 gram of pitch in 100 ml of solvent for one hour, and determining the amount of the undissolved material collected on a fritted porcelain filtering crucible. In tests with high boiling point solvents such as quinoline and nitrobenzene, the sample was digested only (no refluxing) in the solvent at 80-90° C on a steam bath. The results of solubility tests on five coal-tar pitches ranging in melting point from 92 to 180° C are shown in Table 1.

TABLE 1

SOLUBILITY OF PITCH IN SOLVENTS

Solvents	Percent Solubility					
	92° C Pitch	100° C Pitch	108° C Pitch	127° C Pitch	180° C Pitch	Average
Quinoline	71	93	90	82	71	81
Nitrobenzene	66	88	84	67	57	72
Pyridine	61	88	82	67	59	71
Chloroform	52	68	68	55	46	58
Toluene	53	70	68	53	44	58
Benzene	50	67	66	56	40	56
Carbon Tetrachloride	45	58	54	38	27	44
Acetone	44	56	50	31	28	42
Butyl Alcohol	33	40	39	27	19	32
n-Heptane	25	25	22	15	7	19
Isopropyl Alcohol	20	27	22	11	7	17
n-Hexane	19	17	15	9	6	13
Methyl Alcohol	16	19	15	7	4	12
Petroleum Ether	10	8	8	9	4	8

Of the solvents examined, quinoline and acetone were selected for various reasons. Quinoline appeared to be the solvent having the strongest dissolving power and, as such, would isolate the least soluble fraction usually referred to as carbon-I. Acetone was chosen because it appeared to provide a fair distribution of the pitch quinoline-soluble portion into two fractions; furthermore, acetone, because of its high volatility, can be driven off easily at low temperature.

Fractionation Procedure

A sample size of 20 grams was found adequate in most cases to provide fractions in sufficient quantity to permit their analysis.

Hard binders were ground to pass a 65 mesh sieve. Soft binders were slightly heated for easier manipulation.

Acetone-Soluble Fraction

Since it was inconvenient to carry out the extraction in one operation on account of the considerable quantity of acetone, equivalent to the proportion employed in the solubility tests, successive extractions were carried out to complete the separation of the acetone-soluble fraction. With 20 grams of starting binder material, three extractions, with 500 ml of acetone each, were generally sufficient. Between extractions, the acetone solution was filtered off, the residue washed with acetone and dried. During the first, and occasionally also during the second extraction, part of the pitch softened and formed agglomerates; consequently it was necessary to grind the residue between extractions. Soxhlet extraction was attempted on a few pitches, but the agglomeration was even worse. The filtration was carried out on a specially made aluminium filter support with a detachable top light enough to be weighed on an analytical balance. A combination of a double layer of glass-fiber filter paper and one analytical filter paper disk was used as filtering medium.

To recover the acetone-soluble portion from the filtrates and washings, the bulk of the acetone was removed by careful distillation. Occasionally, the solution showed tendency to bump, even when "Boileezer" stones were added; it was therefore preferable to remove the acetone simply by slow evaporation. In either case, the concentrated solution was finally transferred to a tared vessel and the remaining acetone removed by evaporation in a vacuum oven.

Quinoline-Insoluble Fraction

The residue from the acetone extraction was ground to a fine powder in a glass mortar and digested with quinoline on a steam bath while stirring. In the preliminary work, a constant amount of quinoline was used for all pitches. However, it was observed that the filtration rate varied, depending on the pitch type, from fast to zero; the filtration was especially difficult with heat-treated or cut-back pitches. This difficulty was overcome, and fast filtration obtained, by using a quantity of quinoline proportional to the expected percentage of the intermediate fraction (quinoline-soluble, acetone-insoluble); this percentage was calculated by deducting from the known acetone-insoluble content, the amount of quinoline-insoluble determined by an analytical standard procedure on a small sample.

For filtration, the same type of filtering set-up as specified for the acetone-soluble fraction was used. The quinoline-insoluble residue was washed with quinoline and acetone, dried and weighed.

Quinoline-Soluble, Acetone-Insoluble Fraction

The recovery of this intermediate fraction from the filtered quinoline solution presented some difficulty. It was found impossible to get rid completely of the quinoline by distillation at atmospheric pressure or even under vacuum without excessive heating of the residue. A procedure was finally worked out whereby the bulk of the quinoline was first removed by gentle distillation at atmospheric pressure, followed by evaporation in an open dish on a steam bath until a suitable concentration was attained. The concentrated solution was then poured slowly while stirring into acetone; the extent to which the quinoline solution was concentrated prior to precipitation, and the volume of acetone used were proportional to the amount of solute. A dense, almost crystalline precipitate formed which was easily filtered. After filtration, it was ground to a fine powder, re-extracted with acetone, re-filtered and dried. After this treatment, there was no trace of quinoline odour and it was assumed that the solvent was completely removed. Because of practical difficulties, no attempt was made to recover the very small amount of solute which remained in the filtrate.

A flow diagram illustrating the complete fractionation technique is given in Figure 1.

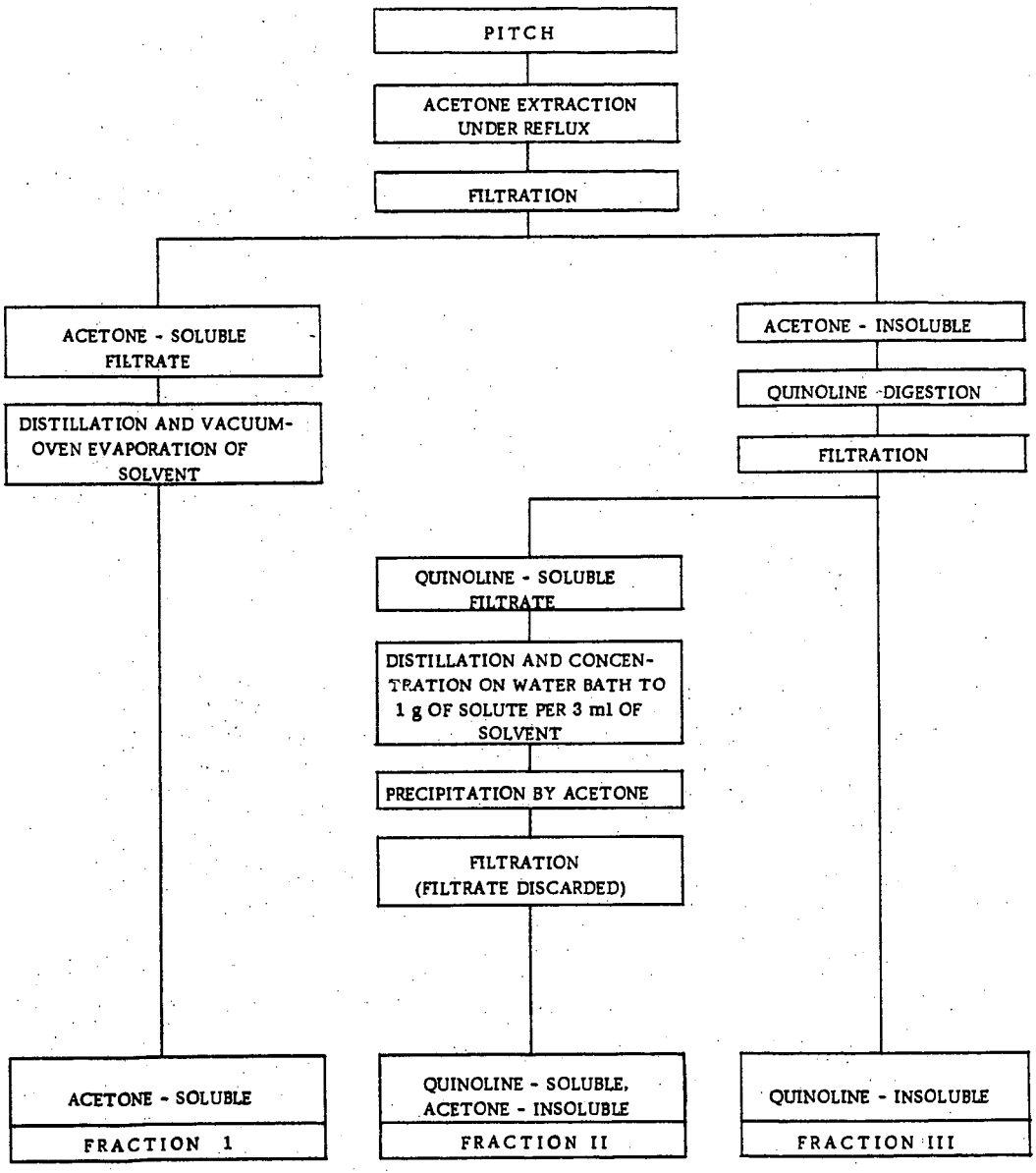

FIGURE 1

FRACTIONATION SCHEME

RESULTS

The samples of binder pitch selected for this investigation represented different types of pitch, different producers and different levels of quality. They are listed in Table 2 which also contains some of their properties.

In all, 26 samples were fractionated: 14 straight-distilled pitches; three heat-treated pitches; six cut-back pitches, i.e. pitches which had been produced by blending heat-treated pitches with some light materials such as oil or tar; one chemically-treated pitch prepared from straight-distilled pitch by digesting with 2% sulphur; and finally two petroleum pitches. Twelve additional regular production petroleum pitches, all from the same source, were also fractionated, but only one is reported since identical observations were made on all. Consequently, it should be borne in mind that conclusions drawn and observations made on regular production petroleum pitches are based effectively on a fairly large number of samples and not only on sample J-1.

Fractionation results and some characteristics of pitch fractions are presented in Table 3.

DISCUSSION

Acetone-Soluble Fraction

The acetone-soluble fraction is a dark brown, almost black material which at room temperature has a consistency ranging from that of tar or very heavy grease to that of solid pitch. Thus, there is a noticeable difference in viscosity for fractions obtained from different pitches, as shown by the equiviscous temperatures given in Table 3. The coking value of the fraction is low, but also covers a fairly wide range; in general, it is lower for cut-back binders than for straight-distilled pitches of equivalent softening point. It is also of some interest to note that the coking value of the acetone-soluble fraction for regular production petroleum pitches, exemplified by sample J-1, is higher than for any of the coal-tar pitches, although the carbon-hydrogen ratio is significantly lower.

Only the acetone-soluble fraction was found suitable for viscosity determination. As shown in Figure 2, there is a definite trend for the temperature coefficient of whole pitches to decrease with larger differences between the equiviscous temperature at 15 poises of the whole pitch and that of the acetone-soluble. The only real exception is the experimental petroleum sample J-2; difficulty experienced with this pitch in preparing mix for test electrodes might be explained at least in part by this deviation, which is the result of the very low equiviscous temperature of the acetone-soluble as compared to the high equiviscous temperature of the whole pitch. On the basis of present knowledge, it can be hypothesized that this petroleum pitch was produced by severe cracking of a petroleum crude and dilution of the residuum with light material to obtain the desired melting point.

The relationship between coking value of the acetone-soluble fraction and its equiviscous temperature, shown in Figure 3, illustrates some interesting facts. The acetone-soluble fractions of four of the six cut-back pitches are characterized by low coking value - approximately 15% - and low equiviscous temperature - approximately 52° C. Considering the melting point level of these pitches, it can be reasonably assumed from this relationship that they were produced by diluting high softening point binders presumably with very light materials such as "oils"; this is a process by which binders of low quality can be expected to result. Straight-distilled pitch C-2 also contains an acetone-soluble fraction exhibiting low coking value and low equiviscous temperature, and yet is not a cut-back pitch; in this instance, it should be remembered that the softening point of C-2 is very low compared to those of cut-back pitches mentioned above and consequently, there is no discontinuity between the acetone-soluble characteristics and those of the whole pitch. Samples A-4 and C-7 are also cut-back pitches, but the material used for diluting was tar, which explains the higher figure for coking value and equiviscous temperature of their acetone-soluble.

Quinoline-Soluble, Acetone-Insoluble Fraction

The quinoline-soluble, acetone-insoluble fraction consists of a black-brown brittle substance which can be pulverized easily. Upon heating, it does not melt although it shows some tendency to fuse. Its carbon-hydrogen ratio is somewhat higher than that of the whole binder, and does not show much variation; there is, however, a noticeable difference between the fractions from binders of coal-tar and petroleum origin, the latter having a lower carbon-hydrogen ratio. The same applies to the coking value; it is lower for petroleum pitches, with the exception of the experimental one, than for binders of coal-tar origin.

TABLE 2

DESCRIPTION OF PITCH SAMPLES

Sample Identification[a]	Compressive Strength of Test Electrodes kg/cm^2	Melting Point °C	Coking Value %	C-I (Quinoline-Insoluble) %	Atomic Carbon-Hydrogen Ratio	Density g/cc	Viscosity Data[b] EVT_{15}	Viscosity Data[b] EVT_{1015}	Viscosity Data[b] Temperature Coefficient poises/°C
COAL-TAR STRAIGHT-DISTILLED PITCHES									
A-1	430	111	61.6	14.0	1.97	1.35	162	123	25.6
B-1	382	109	59.8	15.7	1.91	1.36	165	124	24.4
C-1	365	95	57.7	16.7	1.93	1.35	149	108	24.4
D-1	361	108	59.4	23.1	1.84	1.36	170	126	22.7
E-1	360	107	59.4	13.7	1.85	1.34	158	118	25.0
F-1	354	108	58.2	9.9	1.72	1.33	166	127	25.6
C-2	354	50	44.5	13.4	1.76	1.28	86	54	31.2
C-3	351	112	56.2	6.5	1.80	1.32	172	131	24.4
A-2	347	95	55.5	3.4	1.74	1.32	149	114	28.6
G-1	320	100	53.1	7.4	1.68	1.30	150	110	25.0
G-2	320	88	53.5	10.0	1.82	1.32	141	102	25.6
H-1	296	69	44.1	6.8	1.66	1.24	111	78	30.3
C-4	274	93	51.4	5.8	1.73	1.33	147	110	27.0
I-1	257	93	49.7	4.9	1.62	1.31	147	111	27.8
COAL-TAR HEAT-TREATED PITCHES									
C-5	444	138	65.6	14.2	1.86	1.33	207	158	20.4
A-3	410	129	67.3	21.3	1.92	1.35	204	152	19.2
C-6	339	102	56.8	11.5	1.78	1.32	162	119	23.2
COAL-TAR CUT-BACK PITCHES									
A-4	376	102	56.0	14.2	1.67	1.32	162	121	24.4
C-7	354	105	57.2	9.8	1.79	1.32	166	125	24.4
I-2	313	104	55.7	14.2	1.68	1.32	170	123	21.3
I-3	309	104	53.9	18.9	1.69	1.33	158	115	23.2
I-4	275	102	56.5	17.9	1.70	1.32	166	115	19.6
A-5	165	107	60.9	28.9	1.80	1.34	175	117	17.2
COAL-TAR CHEMICALLY-TREATED PITCH									
A-6	246	100	49.6	4.7	1.59	1.30	153	115	26.3
PETROLEUM PITCHES									
J-1 regular production	300	109	55.6	19.0	1.46	1.28	166	127	25.6
J-2 experimental	-	132	56.7	14.6	1.49	1.30	209	155	18.5

(a) Letters indicate different suppliers.

(b) EVT refers to equiviscous temperature i.e. the temperature at which a pitch has a specified viscosity. EVT_{15} and EVT_{1015} correspond to viscosities of 15 and 1015 poises respectively.

Temperature coefficient of viscosity is obtained from the following expression: $1000/(EVT_{15} - EVT_{1015})$.

Note: Analytical data were obtained by Aluminium Laboratories Limited internal methods.

TABLE 3

FRACTIONATION RESULTS AND CHARACTERISTICS OF FRACTIONS

Sample Identification	% Fraction			% Coking Value			Atomic C/H			Density, g/cc			EVT_{15}, °C
	I	II	III	I	II	III	I	II	III	I	II	III	I
COAL-TAR STRAIGHT-DISTILLED PITCHES													
A-1	44.1	42.8	13.1	26.8	88.4	98.8	1.60	2.03	4.26	1.24	1.37	1.62	72
B-1	46.0	39.1	14.9	20.5	90.4	98.9	1.54	2.04	4.55	1.20	1.43	1.63	66
C-1	47.1	37.3	15.6	20.4	88.8	97.9	1.58	2.01	4.03	1.23	1.37	1.60	63
D-1	48.4	29.5	22.1	22.8	89.2	97.9	1.41	1.91	4.26	-	1.34	1.62	79
E-1	47.4	39.2	13.4	22.2	89.4	99.1	1.56	1.96	4.48	1.23	1.39	1.63	74
F-1	51.9	38.4	9.7	24.8	87.5	97.0	1.49	1.94	4.52	1.23	1.39	1.65	79
C-2	61.0	25.7	13.3	16.4	87.3	97.6	1.50	2.01	4.27	1.21	1.38	1.63	40
C-3	49.9	44.1	6.0	22.2	91.2	96.6	1.50	2.06	4.18	1.22	1.39	1.63	66
A-2	56.2	40.5	3.3	21.7	91.0	97.7	1.54	2.04	4.20	1.22	-	-	72
G-1	57.4	35.6	7.0	23.5	91.1	97.0	1.45	1.95	3.77	1.23	1.37	1.59	80
G-2	54.2	36.8	9.0	19.7	90.7	98.6	1.50	2.00	4.05	1.23	-	-	62
H-1	67.2	26.8	6.0	19.0	88.8	99.1	1.44	1.90	3.73	1.21	-	-	58
C-4	57.7	37.1	5.2	20.3	90.5	97.3	1.51	2.03	3.77	1.23	1.40	1.61	69
I-1	60.9	34.0	5.1	20.0	90.9	97.1	1.42	1.98	3.40	1.21	1.38	1.55	63
COAL-TAR HEAT-TREATED PITCHES													
C-5	42.9	44.8	12.3	26.6	91.7	96.0	1.56	2.05	2.96	1.26	1.33	1.51	93
A-3	37.1	43.5	19.4	19.1	92.8	96.4	1.58	2.15	3.19	1.23	1.39	1.52	77
C-6	51.5	38.2	10.3	20.3	93.2	98.7	1.50	2.07	2.95	1.21	1.39	1.50	67
COAL-TAR CUT-BACK PITCHES													
A-4	52.8	34.6	12.6	21.9	91.3	96.9	1.43	1.97	2.52	1.21	1.37	1.44	63
C-7	51.6	40.0	8.4	19.3	92.0	96.4	1.54	2.13	3.30	1.22	1.29	1.55	68
I-2	49.9	36.5	13.6	14.9	93.1	97.4	1.40	1.95	2.62	1.20	1.26	1.46	51
I-3	52.6	29.9	17.5	16.1	93.4	98.0	1.45	1.93	2.48	1.19	1.26	1.44	53
I-4	50.3	33.5	16.2	16.3	92.0	98.3	1.42	2.00	2.55	1.20	1.22	1.28	54
A-5	44.5	27.7	27.8	14.4	94.3	97.9	1.49	2.12	2.54	1.22	1.37	1.45	53
COAL-TAR CHEMICALLY-TREATED PITCH													
A-6	59.4	36.8	3.8	19.9	88.0	94.5	1.47	1.88	3.25	1.20	-	-	69
PETROLEUM PITCHES													
J-1	53.9	25.7	18.4	27.4	83.4	96.1	1.20	1.58	3.01	-	1.35	1.51	72
J-2	47.3	39.0	13.7	18.1	92.0	97.0	1.16	1.78	2.46	1.14	1.31	1.51	45

I = Acetone-Soluble.

II = Quinoline-Soluble, Acetone-Insoluble.

III = Quinoline-Insoluble.

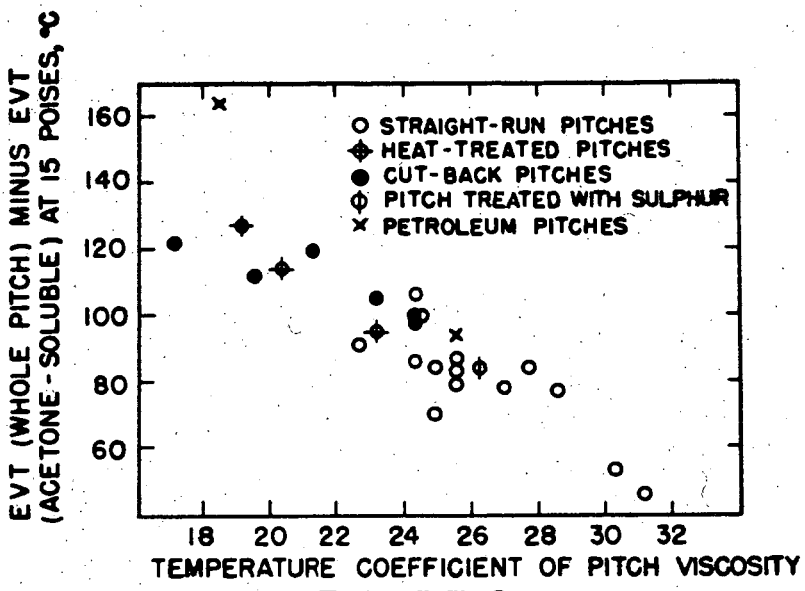

FIGURE 2

RELATIONSHIP OF VISCOSITY DATA OF WHOLE PITCH AND ACETONE-SOLUBLE FRACTION

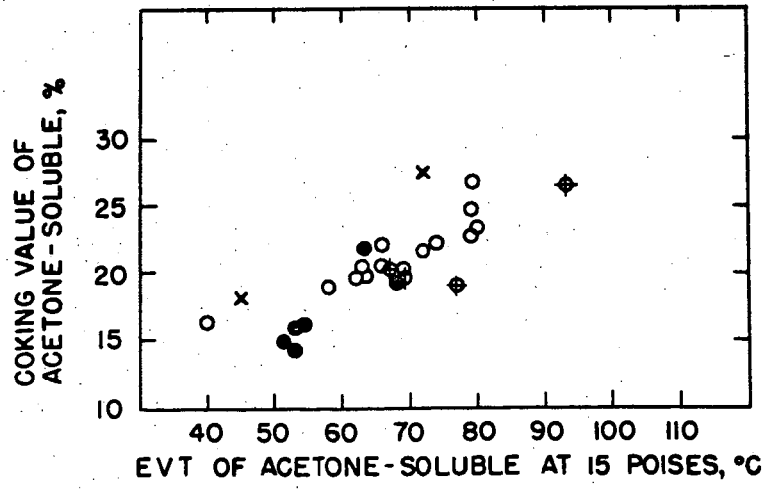

FIGURE 3

RELATIONSHIP OF VISCOSITY DATA TO COKING VALUE OF ACETONE-SOLUBLE

Quinoline-Insoluble Fraction

The quinoline-insoluble fraction is a black, very fine powder. Upon heating it does not show any sign of melting or fusing; it remains practically unchanged in appearance even when heated to 500° C. Its coking value is very high (over 95%), and shows no significant variation for the different pitches. These characteristics would suggest an almost inert material if it were not for its carbon-hydrogen ratio which varies considerably; this constitutes an interesting property which permits significant comparisons between the various pitches. For instance, the carbon-hydrogen ratio of the quinoline-insoluble of all straight-distilled pitches except one are above, or close to, 4.0; the low carbon-hydrogen of the exception (I-1) might well reflect a significant variation in the production and possibly processing of the tar; at the time this sample was produced, pitches from the same source were not considered satisfactory for carbon electrode manufacture in actual plant operation. On the other hand, for straight-distilled pitches which have been subjected to some thermal treatment such as samples C-5, A-3, and C-6, the carbon-hydrogen of the quinoline-insoluble shows a large decrease. This is probably the result of transformation of part of the quinoline-soluble, acetone-insoluble fraction into a type of quinoline-insoluble having a lower carbon-hydrogen ratio than the normal quinoline-insoluble of straight-distilled pitches. The same applies to cut-back binders prepared from heat-treated, high-melting pitches; thus the variation in carbon-hydrogen of the quinoline-insoluble can be very useful in differentiating types of pitches. It can also be observed from Table 3 that density of quinoline-insoluble fraction, is higher for straight-distilled pitches than for treated or cut-back pitches, and follows well carbon-hydrogen ratio with one exception, No. I-4; no explanation can be offered for this apparently abnormal result. This relationship between density and carbon-hydrogen ratio is much better defined for the quinoline-insoluble fraction than for the other two fractions or the whole binder.

Evidence of the presence of different types of quinoline-insoluble particles was found from microscopic examination of quinoline-insoluble fractions from different types of pitches. It was observed that the quinoline-insoluble of straight-distilled pitches consists of very fine particles, of the order of one micron, while in heat-treated and cut-back pitches the insoluble is a mixture of very fine particles and of particles of ten microns and larger; the shape of the particles is also different.

Relationship to Pitch Quality

Although it is logical to assume that fraction characteristics must have some bearing on pitch quality, no significant relationship could be established between any single characteristic and compressive strength of test electrodes which was taken as quality criterion in the investigation described herein. The only fraction which showed some promise was the quinoline-insoluble.

Examination of compressive strength and per cent quinoline-insoluble for straight-distilled pitches (see Tables 2 and 3) indicates a definite trend for higher compressive strengths to be associated with higher quinoline-insoluble contents. However, this does not hold if we examine the different types of pitch together. For instance, cut-back pitch A-5 has the highest quinoline-insoluble of all pitches and yet its corresponding compressive strength is by far the lowest. This is not altogether unexpected, since it can be easily visualized that there must be a limit to the amount of quinoline-insoluble which can be tolerated in a binder. However, this limit seems to vary for different types of pitches; for instance, straight-distilled pitch D-1 contains only a few per cent less quinoline-insoluble than cut-back pitch A-5 and yet its compressive strength is much higher. This might be explained by the large difference in carbon-hydrogen ratio of their respective quinoline-insoluble fraction, 4.3 as compared to 2.5.

It can also be visualized that there exists an optimum percentage for the quinoline-insoluble fraction. Out of mere curiosity compressive strength versus per cent quinoline-insoluble was plotted for approximately 175 pitch samples of different types and from different sources. The curve showed a maximum for compressive strength at approximately 14% quinoline-insoluble; this is roughly the quinoline-insoluble content of most of the best straight-distilled pitches shown in Table 3.

From all these observations made on the quinoline-insoluble fraction, it can be said with a reasonable degree of confidence that this fraction is of some importance in the performance of a pitch as binder. As mentioned earlier, its concentration alone is of little use if pitches of different types are considered. However, by a suitable combination of the amount of the quinoline-insoluble fraction and its carbon-hydrogen ratio and by assuming an optimum percentage - let us say 14% - it might be possible to arrive at a factor which, along with other characteristics of pitch or pitch fractions such as viscosity and coking value, might prove valuable for pitch characterization.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contribution of Messrs. L. Tremblay and R. Beaulieu for carrying out a considerable number of tests in the course of the investigation. They also express their appreciation to the various pitch producers who supplied the experimental samples, and make grateful acknowledgement to Aluminium Laboratories Limited for permission to publish.

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THE RELATIONSHIP BETWEEN THE CONSISTENCY OF THE GREEN ELECTRODE MIX AND THE PROPERTIES OF TEST ELECTRODES

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Introduction

In the panel discussion that followed the symposium on "Tars, Pitches and Asphalts" at the 1959 spring meeting of the American Chemical Society in Boston, members of the panel emphasized that more attention should be given to the measurement and study of the rheological properties of green electrode mixes.

Because of widespread interest in this subject, a preliminary research program was initiated at the Applied Research Laboratory of the United States Steel Corporation to investigate the relationship between the consistency of the green mix and the crushing strength and volume electrical resistivity of specimen electrodes. Consistency has been defined as that property of a body that tends to resist deformation.[1)]* In this paper, consistency is defined more specifically as the torque required to shear the green mix at a constant rate and temperature.

A careful search of the Chemical Abstract indexes covering a 53-year period from 1907 to 1960 revealed that no information has been published on the relationship between the consistency of the green mix and the properties of test electrodes. Only one reference[2)] was found that described an instrument for quantitatively measuring the consistency of green electrode mixes. This instrument, Russian-built, is simply a cone penetrometer that has been modified to measure the pressure (limiting shear stress) required to drive a standard cone, under constant force, into the test mixture to a full stop. Although this instrument has many desirable features, such as simplicity of design and operation, it was not precise or sensitive enough for use in the present investigation. Subsequently, a technical brochure[3)] indicated that another instrument, the Brabender Plastograph, had the desirable characteristics, and was used in the ensuing investigation.

This paper describes the evaluation of rheological properties of green mixes prepared from two coal-tar pitch binders and the properties of the test electrodes made from them. It is hoped that this information will provide a better understanding of the relationship between the rheology of the green mix and electrode performance.

Experimental

For this preliminary study two electrode binders and a calcined petroleum coke were used. The more common properties of the binders are shown in Table I. Both binders were produced in full-scale equipment from the same feed stock. Binder A, a pitch of demonstrated utility, was produced by continuous vacuum-flash distillation. Binder B was specially processed to have essentially the same softening point as Binder A, but a viscosity and a β-resin content significantly higher.

With the exception of the viscosity, standard test methods common to the aluminum and carbon industries were used to measure the properties of the binders. The absolute viscosity of the binders was determined by a Brookfield Synchro-Lectric Viscometer equipped with a 12-inch spindle extension. A special device for heating

* See References.

the air in contact with the pitch and the spindle was used with this instrument. A schematic drawing of the assembled apparatus is shown in Figure 1. The air heater was used to reduce the unwanted drag or torque exerted on the rotating spindle by the "skin" of pitch that has a tendency to form on the surface of the test sample when it is exposed to air at room temperature.

Selected properties of the petroleum coke, used by the Laboratory as a standard, are shown in Table II. The coke was calcined at 1300 C by the supplier and then graded at the Laboratory into the six fractions shown in the table. Because the fractions were sized relative to the dimensions of our laboratory-scale electrode-baking apparatus, they are smaller than the fractions used commercially.

Since the experimental procedures are somewhat involved, the major steps are briefly outlined below. A more detailed discussion of the various procedures will follow.

1. A series of green mixes containing from 31 per cent to 38 per cent binder was prepared in a Brabender Plastograph.

2. The consistency of each mix was measured in the Plastograph as the mix was being prepared.

3. Each batch of green mix was then baked in accordance with a standard Laboratory procedure to yield small test electrodes.

4. The electrodes were tested for crushing strength and volume electrical resistivity.

The Brabender Plastograph, used to prepare the green mixes and measure their consistencies, is shown in Figure 2. The instrument was purchased from C. W. Brabender Instruments Inc., South Hackensack, New Jersey. The sigma blades in the mixing head (1) are driven by a dynamometer (2), which is suspended between floating bearings (3). The torque produced by the blades as they turn in the material at a constant rate of shear is transmitted to the dynamometer. The dynamometer translates the torque through a series of balance levers (4) to a direct-reading balance (5), which is calibrated to indicate the torque in meter-gram units. A strip chart (6) provides a continuous record of the consistency in terms of meter-gram units. Excessive movement of the lever system is dampened by an oil dash pot (7).

The mixing head has a working capacity of 650 milliliters. It is heated by recirculating hot oil from a constant-temperature bath (8) through a jacket that surrounds the mixing head. A special insulated lid (9), not supplied by the manufacturer of the instrument, minimizes the loss of heat from the head and was indispensable as an aid in maintaining the mix at a uniform temperature. Through a small opening in the lid, 5/8 inch in diameter, coke additions can be made without removing the lid.

As mentioned above, green mixes containing from 31 per cent to 38 per cent binder were prepared and their consistencies measured. The composition of a typical batch of green mix is shown in Table III. In this batch, 462 grams of the various coke fractions were blended, as described below, with 238.0 grams (34 weight per cent) of Binder A to yield 700 grams of mix. In all the mixes, the total amount of the two components was held constant at 700 grams.

In the preparation of a typical mix, the calculated amount of molten binder, at a temperature of about 155 C, is added to the preheated mixing head. After the binder has mixed for exactly 7 minutes, the preheated (to 155 C) 10- to 30-mesh coke

fraction is added through the opening in the insulated lid. The remaining fractions are then added in the order of decreasing size at 5-minute intervals. The addition of these fractions is illustrated in Figure 3. Mixing is continued at 155 C for 30 minutes after the addition of the last (minus 325-mesh) coke fraction. The torque reading, in meter-grams, at the end of this mixing period is recorded as the consistency of the mix.

The change in consistency that occurs as the various coke fractions are added to the binder is illustrated by the typical consistency curves that are reproduced in Figure 4. Reading from right to left, the steps in the curve represent the increase in consistency that occurs as the six coke fractions are added to the binder at 5-minute intervals. The position of the left extremity of the curve defines the consistency of the mix. The sensitivity of the instrument to the change in consistency brought about by the addition of the various coke fractions is clearly indicated. The second curve in this figure was included to demonstrate the excellent repeatability of the instrument over the entire consistency range.

After measuring the consistency, the green mixes were packed into perforated graphite molds, Figure 5, and baked to a temperature of 1000 C in 24 hours. The baked electrodes were then tested for crushing strength and electrical resistivity. The procedure for preparing, baking, and testing specimen electrodes was described in a paper[4] presented at the Spring 1959 meeting of this Division.

Results and Discussion

To make clear the relationship between the consistency of the various green mixes and the properties of the test electrodes, the experimental data were plotted in bar-chart form. The relationship between the consistency and crushing strength for both binders is illustrated in Figure 6. The black bars represent the consistency of the mix at various levels of binder concentration, and the white bars show the crushing strength of specimen electrodes prepared from green mixes containing various percentages of binder. The number at the top of each bar represents the percentage of binder in the mix. From this chart, it is evident that an excellent correlation exists between the consistency of the green mix and the crushing strength of the test electrodes. It is extremely interesting to observe that, as the percentage of binder increases within the limits shown, the consistency and crushing-strength values for each binder pass through a maximum simultaneously. This relationship suggests that the consistency of a green mix can be measured to determine the optimum percentage of binder to use in the preparation of an electrode with maximum crushing strength. For Binder A, for example, a maximum consistency value was obtained at a binder concentration of 34 per cent. This mix in turn produced an electrode with the highest strength. Therefore, the optimum percentage of binder is 34 per cent.

This chart also shows that Binder B, which had been processed to have a higher viscosity than A, yielded mixes with consistencies significantly higher than those of Binder A. In a like manner, Binder B produced electrodes with crushing strengths somewhat higher than those of Binder A. It is also interesting to note that the percentage of binder required to obtain electrodes with maximum strength was about the same for each binder. The fact that a stronger electrode can be obtained with the specially treated binder (Binder B) seems to indicate that the special treatment was indeed very beneficial.

Figure 7 shows the relationship between the consistency of the mix and the electrical resistivity of the electrodes. It is evident that a good correlation also exists between these parameters. For each binder, as the consistency values pass through a maximum the resistivity values pass through a minimum. This relationship

suggests that the consistency of the mix can also be employed to determine the optimum percentage of binder to use in preparing an electrode with minimum electrical resistivity. Binder B produced electrodes with resistivities somewhat lower than those of Binder A. Once again, the beneficial effect of the special treatment was demonstrated.

Summary

The Applied Research Laboratory has studied the relationship between the consistency of the green electrode mix and selected properties of test electrodes. The results of this preliminary investigation suggest that (1) the consistency of the green mix can be used to determine the optimum concentration of binder required to produce electrodes of the highest quality, (2) the Brabender Plastograph, with slight but important modifications, is a suitable instrument for measuring the consistency of green mixes, and (3) for the same concentration of binder in the green mix, an appropriately treated binder will yeild better electrodes than an untreated binder. This investigation is being continued to further verify and extend these findings. It is anticipated that the results of this more extensive study will be presented at a future meeting of this Division.

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Table I

PROPERTIES OF BINDERS

	BINDER A	BINDER B
SOFTENING POINT, CUBE-IN-AIR, C	102.3	105.5
BETA RESINS (BI-QI), wt %	11.9	19.2
SPECIFIC GRAVITY (60 F/60 F)	1.32	1.32
VISCOSITY, CENTIPOISES		
at 140 C	4600	7610
at 150 C	1630	3200
at 160 C	810	1340
IRON, wt %	0.020	0.018
ATOMIC CARBON/HYDROGEN RATIO	1.78	1.77
BENZENE INSOLUBLES, wt %	21.9	28.6
QUINOLINE INSOLUBLES, wt %	10.0	9.4
COKE VALUE, CONRADSON, wt %	55.2	55.4
DISTILLATION, wt %		
to 270 C	0.0	0.0
270 to 300 C	0.2	0.2
300 to 360 C	1.7	2.6
360 to 400 C	10.1	10.1
SULFUR, wt %	0.62	0.59

Table II

PROPERTIES OF CALCINED PETROLEUM COKE

APPARENT DENSITY, GM/CM^3	0.898
CARBON, wt%	97.61
HYDROGEN, wt%	0.24
ASH, wt %	0.35
SULFUR, wt%	1.27
SIEVE ANALYSIS, wt %	
-10 +30 MESH	20
-30 +50 MESH	16
-50 +100 MESH	19
-100 +200 MESH	13
-200 +325 MESH	10
-325 ON PAN	22

Table III

COMPOSITION OF A TYPICAL BATCH OF GREEN MIX

	WEIGHT IN GRAMS	WEIGHT PER CENT OF MIX
BINDER A	238.0	34.0
COKE FRACTIONS		
-10 +30 MESH	92.4	13.2
-30 +50 MESH	73.9	10.6
-50 +100 MESH	87.8	12.5
-100 +200 MESH	60.1	8.6
-200 +325 MESH	46.2	6.6
-325 ON PAN	101.6	14.5
TOTAL	700.0	100.0

Note: Coke fractions are added to the binder in the order of decreasing particle size.

APPARATUS FOR VISCOSITY DETERMINATIONS

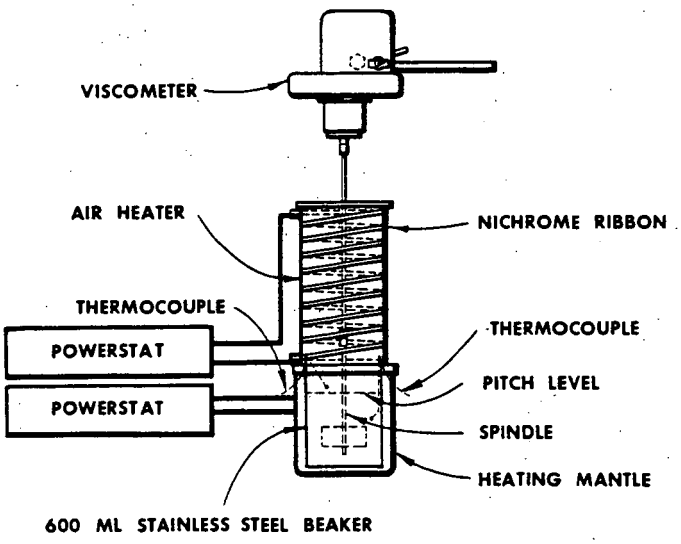

Figure 1. APPARATUS FOR VISCOSITY DETERMINATIONS

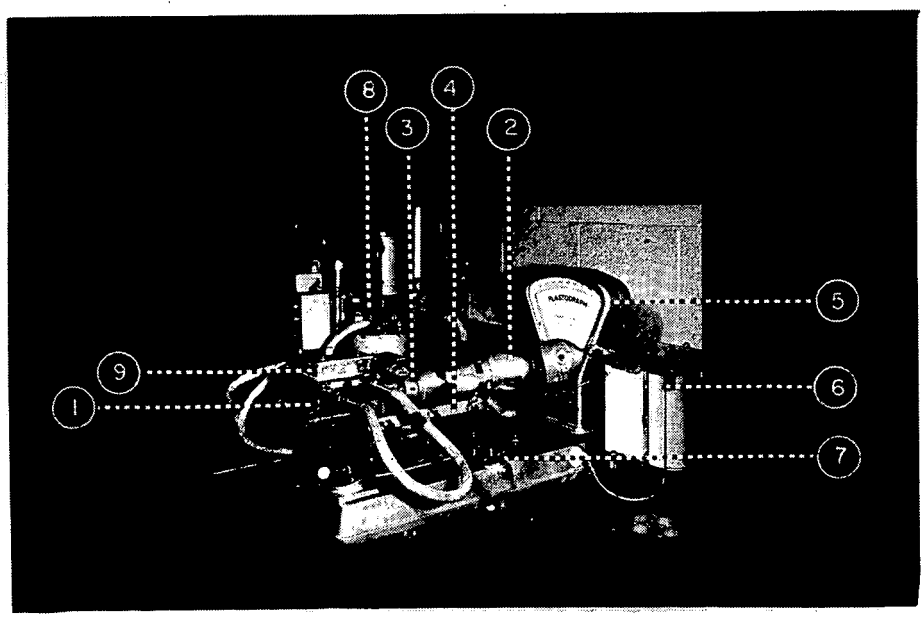

Figure 2. BRABENDER PLASTOGRAPH

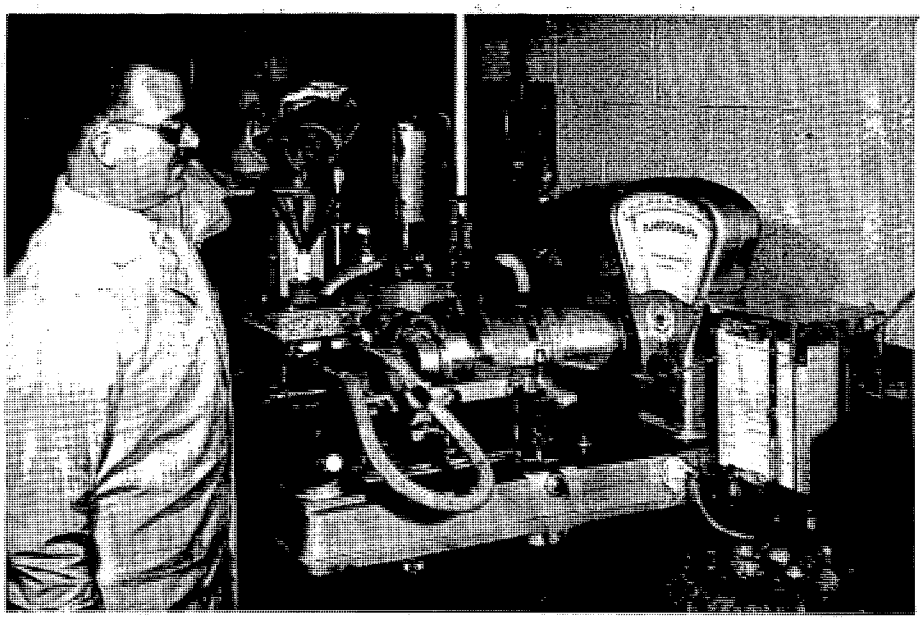

Figure 3. ADDING PETROLEUM COKE FRACTIONS

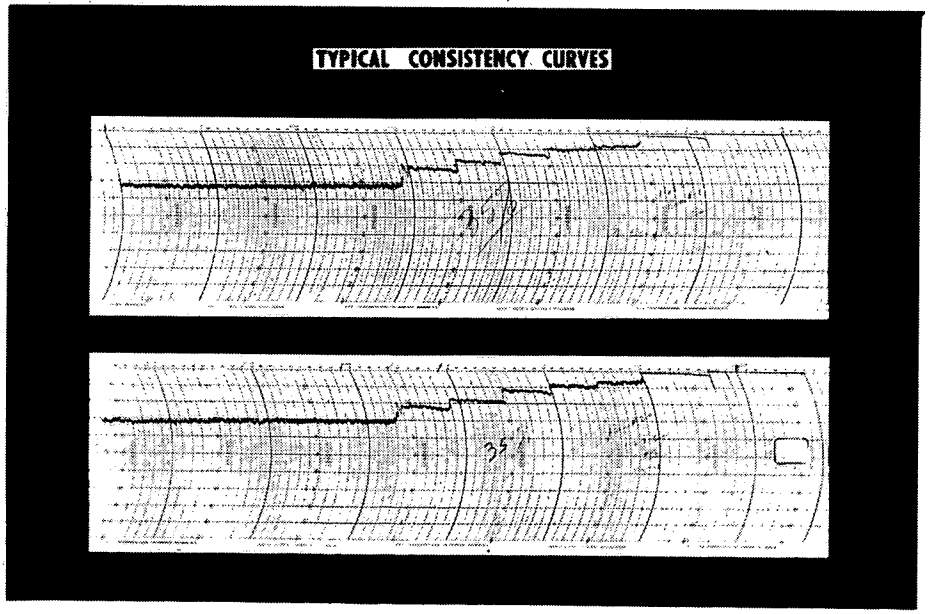

Figure 4. TYPICAL CONSISTENCY CURVES

Figure 5. PACKING THE GREEN MIX

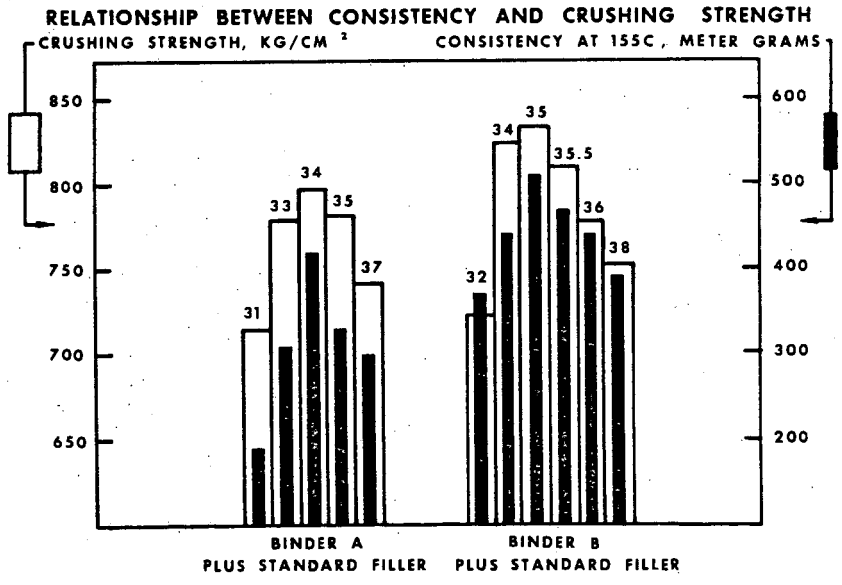

Figure 6. RELATIONSHIP BETWEEN CONSISTENCY AND CRUSHING STRENGTH

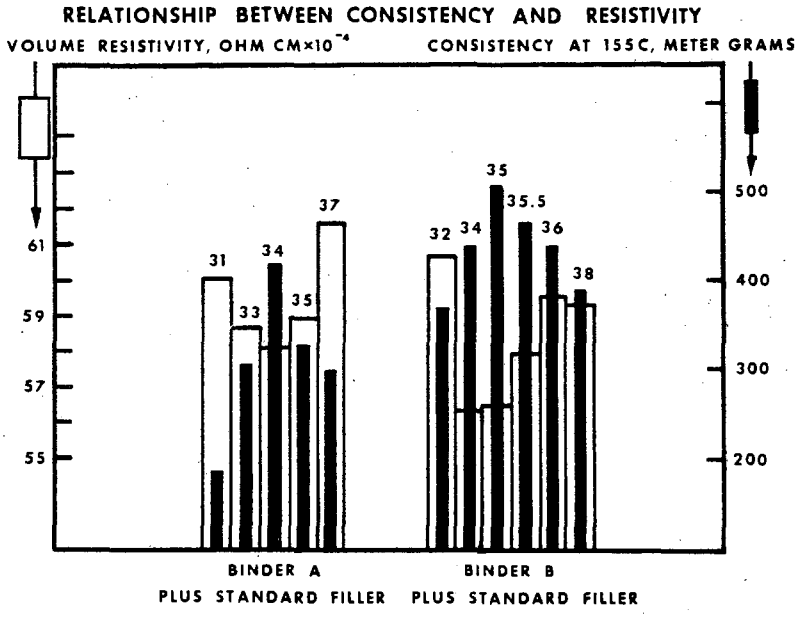

Figure 7. RELATIONSHIP BETWEEN CONSISTENCY AND RESISTIVITY

THE RELATIONSHIP OF PITCH PROPERTIES TO ANODE PROPERTIES

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Introduction

The aim of this report is to provide help in appraising a pitch for suitability as binder in the anodes of the alumina reduction plants. The information was gained from testing over 148 pitches from 21 producers. Commercially available and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches were included.

An indication of the suitability of a pitch as binder is obtained by using as an index the properties of baked electrodes made in the laboratory with the test pitch. The electrodes are prepared using controlled conditions designed to maintain all variables as constant as possible other than the pitch being appraised. The laboratory techniques used produce electrode specimens that have the same level of values for the properties of apparent density, electrical resistivity, total porosity and crushing strength as those produced in the plant from the same materials.

This report (1) is based on the application of this technique to laboratory specimens of Soderberg composition. It furnishes some comparisons of the resulting properties to those of the anodes in the plants. (2) It gives the correlation found between the properties of the laboratory specimens and the analysis of the binder pitch. (3) It furnishes the percentage influence found for the measured pitch properties on variations in the properties of the laboratory-prepared carbon. (4) It provides equations which can be used to predict these properties of the laboratory specimens from the analysis of the binder pitch. Only the common determinations of softening point, coking value, components insoluble in benzene and quinoline, specific gravity and distillate fractions are required. The difference between the predicted and the measured physical properties are generally within the precision of the methods for measuring the properties. These equations can be used as guides by laboratories without facilities for preparing carbon anode specimens, by people with limited experience in evaluating pitches, and by pitch manufacturers in developing binder pitches.

Experimental Results

Comparison of Properties of Laboratory Specimens with Those of Plant Anodes

Table I provides a comparison of the properties of baked carbon of Soderberg composition made of the same materials in the laboratory and in the reduction plant. This one comparison given as an example has been confirmed many times. This agreement between these properties of laboratory specimens and baked plant anodes greatly shortens the time required for a pitch appraisal in terms of these properties--- from soon after the arrival of the pitch sample in the laboratory, contrasted with six weeks or more after using the trial pitch in the Soderberg plant.

Correlation Between Pitch Properties and Properties of Laboratory Specimens.

Having established a technique for duplicating plant anode properties in the laboratory, it was used to determine the correlation between these properties and the properties of the pitch. During the period of 1941-1954, a plant laboratory found the following relationships. With few exceptions, as the softening point, coking value, benzene insoluble, quinoline insoluble, and specific gravity of the pitch increased, the values for anode properties of apparent density and crushing strength

also increased. This was accompanied by a decrease in electrical resistivity and total porosity. These findings differed in two respects from the experience reported by some laboratories during this period. The difference between the amount of benzene and quinoline insoluble components, commonly designated as "beta resins", was not found to have a pronounced correlation with these anode properties. Of special interest was the finding that the half of the specimens which had the highest apparent density and crushing strength and the lowest electrical resistivity and total porosity were made with pitches which had more than 10% of components insoluble in quinoline. At that time some had recommended that purchase specifications should restrict the quinoline insoluble content to a maximum of 10%.

Findings of the plant laboratory for a series of 28 coal tar, petroleum, and experimental pitches, submitted by nine pitch producers, are given in Figure 1. The properties of the anode specimens are arranged in order of increasing apparent density. The properties of the pitch from which each anode was made are listed directly underneath. Instead of drawing the best straight line through the plotted data points, they were connected to adjacent points to show that most of the properties of pitches which were measured are inherently interrelated and strongly affect the properties of the anodes.

This approach to the evaluation of pitches was continued by the Research Laboratory when it began operating in 1955. During a period of four years, 114 additional pitches were tested. This series also included commercial and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches from domestic and foreign producers. The relationships between properties of pitches and anode specimens made with them found by the plant laboratory were confirmed. There was no indication that changes in pitch manufacturing operations nor in sources of supply changed the general relationship of the properties of pitches to laboratory specimens during the 19-year period. To determine to what extent the peaks and depressions in the plotted relationship of pitches and anodes were due to plotting different pitch types, sources of tars, and processes, separate graphs were made for pitches of one type. Figure 2 makes the comparison for nine coal tar pitches from a single vendor during a two-year period. Figure 3 shows the relationship for 12 pitches of petroleum origin. In general, the interrelation of pitch properties and their effect on the laboratory specimens was found to apply to all types of these pitches.

Another Comparison of Laboratory and Plant Experience.

Figure 2 shows a pronounced relationship of the softening point of high-temperature coal tar pitches to anode properties. Additional confirmation that laboratory experiences are translatable into plant experience is furnished in Figure 4. It contains data for plant paste made with three pitches having different softening points. Figure 4 indicates the reproducibility of sample testing and constant quality of plant paste over a three-month period, and the sensitivity of the test method to detect changes in paste induced by changes in the binder. Material used in this series was obtained from routine sampling of plant paste for quality control. It shows how changing from a binder with a softening point of 90°C to one with 110°C resulted in improvement in these properties, to the extent of shifting the range for apparent density from 1.51-1.59 to 1.55-1.65 gms./cu.cm., electrical resistivity from 58-65 to 52-61 ohms/m./sq.mm. and crushing strength from 6,200-7,500 to 6,800-9,000 lbs./sq.in.

Percentage Influence of Measured Pitch Properties on Variations in Properties of Baked Laboratory Specimens.

A multiple correlation was made to determine quantitatively the effect of each of these properties of the binder on those of the baked carbon. Data was processed from 455 specimens representing 51 pitches of all types tested over a two-year period. This series of pitches produced laboratory specimens with a range in properties of

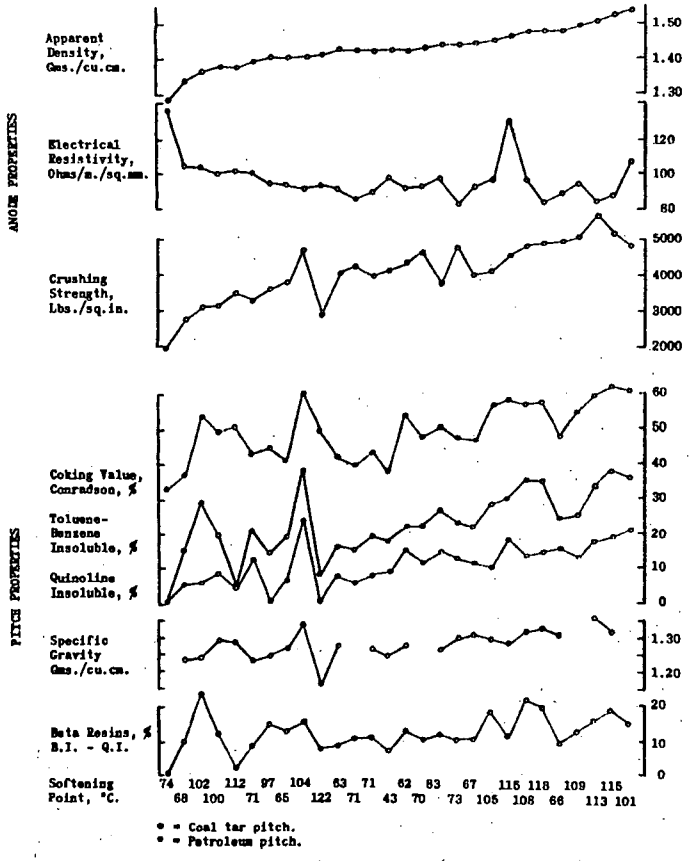

FIGURE 1. CORRELATION OF THE PROPERTIES OF LABORATORY SODERBERG SPECIMENS WITH BINDER PROPERTIES. BACKGROUND EXPERIENCE 1941-1954.

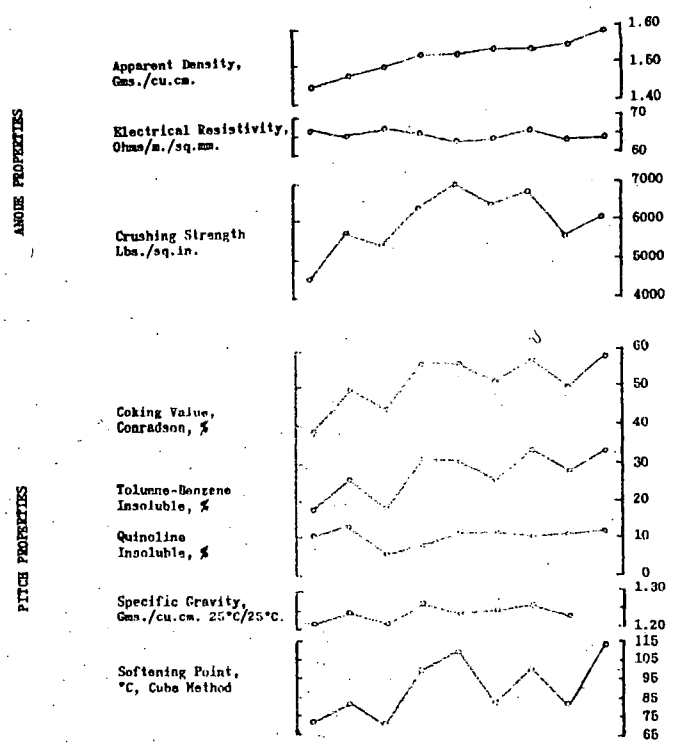

FIGURE 2. CORRELATION OF THE PROPERTIES OF LABORATORY SPECIMENS WITH BINDER PROPERTIES. HIGH TEMPERATURE COAL TAR PITCHES FROM ONE PRODUCER OVER TWO-YEAR PERIOD.

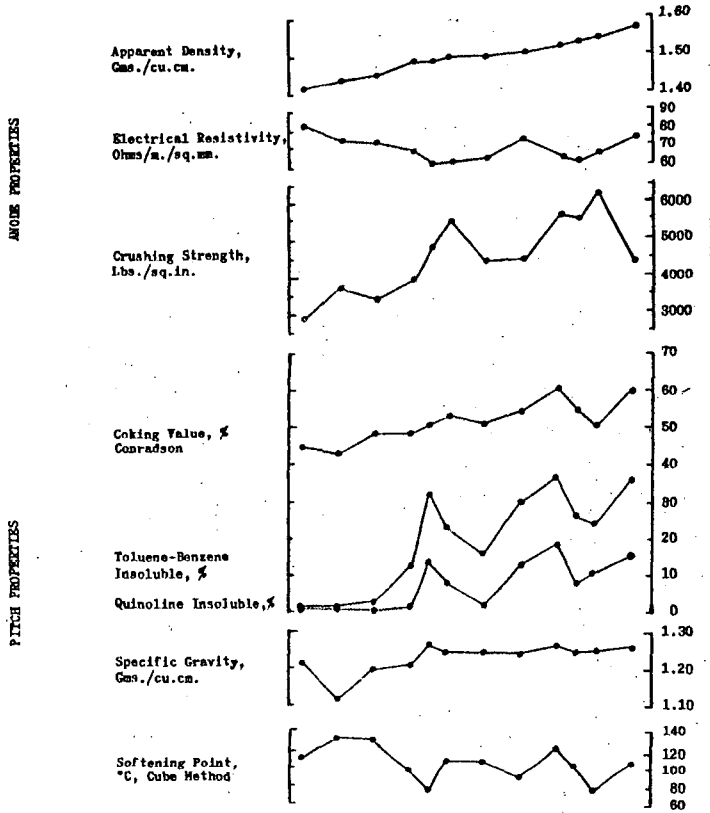

FIGURE 3. CORRELATION OF THE PROPERTIES OF LABORATORY SODERBERG SPECIMENS WITH BINDER PROPERTIES. ASPHALT, OIL, AND GAS PITCHES FROM SIX PRODUCERS.

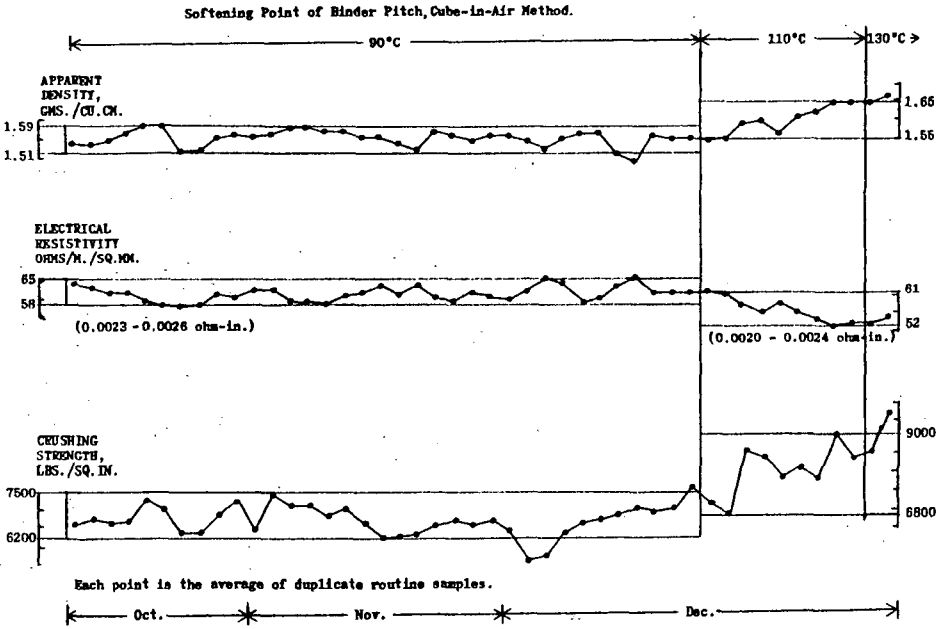

FIGURE 4. APPLICATION OF TESTS TO PLANT PASTE BAKED IN LABORATORY SHOWS REPRODUCIBILITY, SENSITIVITY, AND RELATIONSHIP TO SOFTENING POINT.

1.34 to 1.60 gms./cu.cm. apparent density, 53.3 to 80.9 ohms/m./sq.mm. electrical resistivity, and 2,450 to 7,100 lbs./sq.in. crushing strength. The percentage influence of the measured pitch properties on variations in properties of baked carbon with the constant aggregate, mixing and baking conditions is given in Table II. The multiple correlation coefficients revealed that 83.7% of the variation in apparent density, 64.8% of the variation in electrical resistivity, and 79.6% of the variation in compression strength of baked carbon under these testing conditions are accounted for by variations in the six properties measured.

The correlation of the atomic carbon to hydrogen ratio of the whole pitch to these properties of the laboratory specimens was also made. It was found that its correlation did not significantly improve the predictability of the properties over that obtained with the multiple correlation equations for the six more common determinations.

TABLE I.

COMPARISON OF PROPERTIES OF BAKED ANODES OF SODERBERG COMPOSITION MADE OF THE SAME MATERIALS BY THE LABORATORY AND BY A REDUCTION PLANT

Anode Preparation	Apparent Density Gms./cu.cm.	Electrical Resistivity, Ohms/m./sq.mm.	Compression Strength, Lbs./sq.in.
Samples Cored from	1.56	58.8	6,400
Anodes in a Reduction	1.52	54.7	5,900
Plant	1.55	107.0*	**
	1.55	54.2	**
	1.52	54.5	6,800
	1.54	53.0	7,100
Average	1.54	55.0	6,550
Paste Made in Plant,	1.55	54.4	6,400
Baked in Laboratory	1.52	53.0	7,100
	1.55	54.8	6,200
Average	1.54	54.1	6,600
Paste Made and Baked	1.54	54.6	6,900
in Laboratory	1.54	54.6	6,900
Average	1.54	54.6	6,900

* This high resistivity value indicates that the area sampled in the continuous anode had not completed baking. It was not included in the average.

** These samples were used for other tests and could not be crushed.

Equations for Predicting Properties of Resulting Anode Specimens from the Analysis of the Pitch.

Equations were established by Research personnel which permit the prediction of carbon properties made with the standard mixing and baking conditions. These equations and the methods used for the determination of the six properties of pitch are given in Table III.

The experimentally determined values for apparent density, electrical resistivity and crushing strength for the specimens used to obtain the equations are compared with the values predicted with the equations in Figures 5, 6 and 7, respectively.

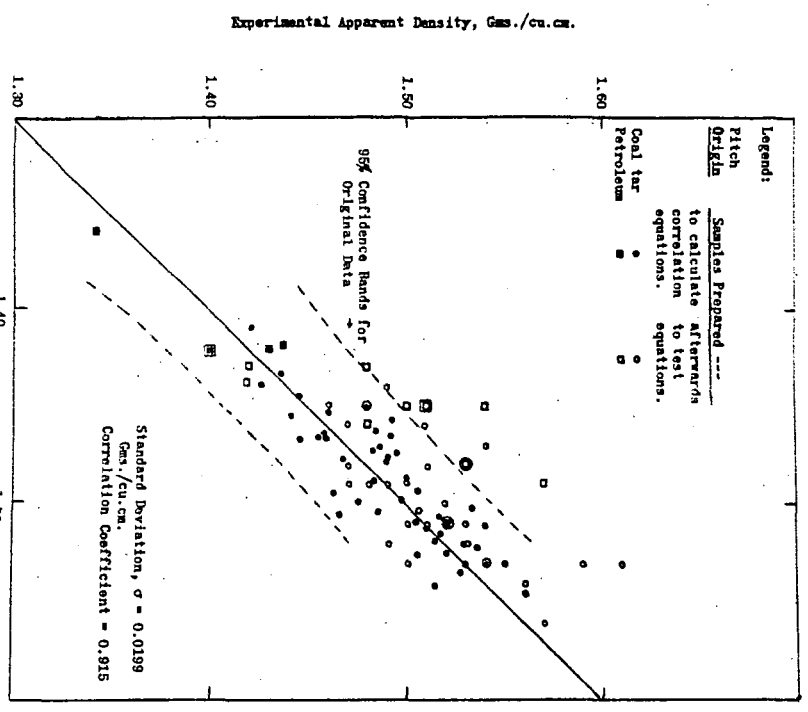

FIGURE 5. THE CORRELATION OF APPARENT DENSITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

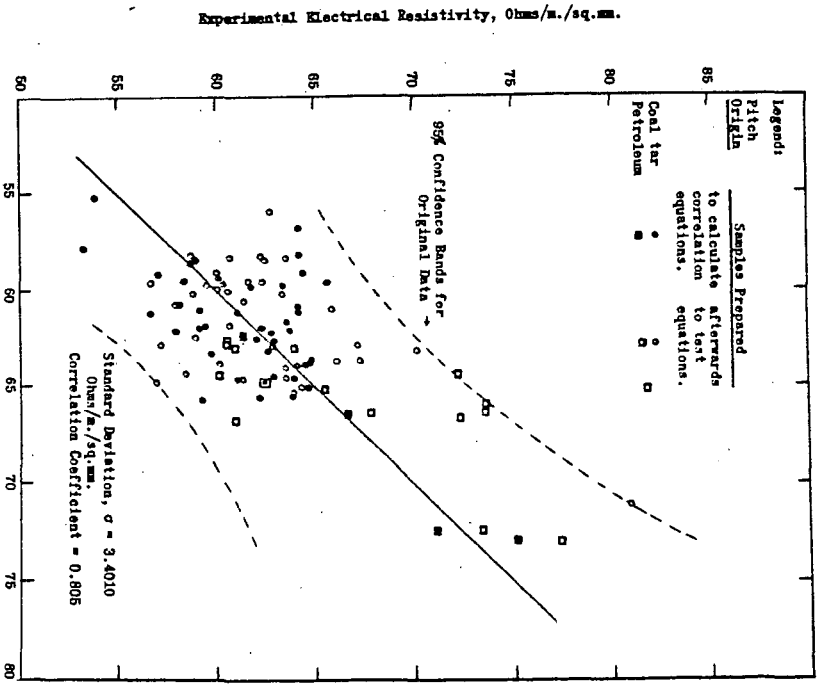

FIGURE 6. THE CORRELATION OF ELECTRICAL RESISTIVITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION

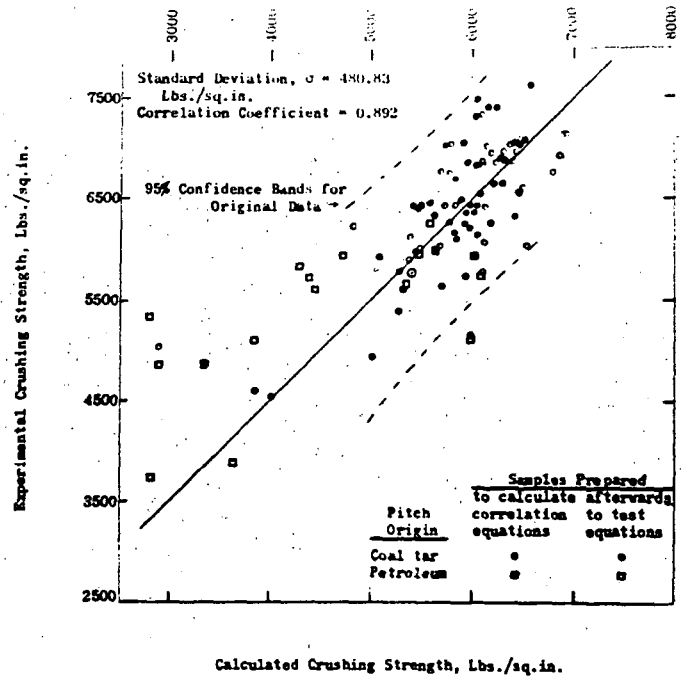

FIGURE 7. THE CORRELATION OF CRUSHING STRENGTH WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

The standard deviations for these measurements of apparent density, electrical resistivity and crushing strength of the specimens made with the standard conditions and commercial and experimental petroleum, oil, gas, asphalt, and regular and low-temperature coal tar pitches were 0.0199 gms./cu.cm., 3.4 ohms./m./sq.mm. and 480.8 lbs./sq.in., respectively. Correlation coefficients of 0.915, 0.805, and 0.892 were found between the predicted and experimental values for apparent density, electrical resistivity, and crushing strength, respectively. These correlation coefficients would have been 1.0 if these equations had been able to account for all the variations in the quality of the carbon.

These equations were applied to 51 additional pitches of all types. These predicted values are plotted against the experimentally determined properties on the same Figures 5, 6 and 7 to test the validity of the equations. In general, the predictions for all types of pitches were within the precision of the test methods for measuring the carbon at the 95% confidence level. The 95% confidence bands drawn on these figures were calculated only for the original 51 pitches used to develop the equations.

These equations are claimed to apply only to the type of coke, aggregate formulation, mixing and baking conditions used in this study. However, there are reasons to believe that they may be adjusted for other cokes and conditions by changing the last constant term of the equations to balance the influence of these factors on carbon properties.

TABLE II.

THE PERCENTAGE INFLUENCE OF MEASURED PITCH PROPERTIES ON VARIATIONS IN PROPERTIES OF BAKED CARBON WITH A CONSTANT AGGREGATE, MIXING AND BAKING CONDITIONS

Pitch Property	Apparent Density	Electrical Resistivity	Compression Strength
Softening Point, °C	21.43	2.98	8.28
Benzene Insoluble, %	0.59	0.39	0.16
Quinoline Insoluble, %	1.17	4.73	0.72
Coking Value, % Conradson	5.44	1.56	1.11
Specific Gravity, gms./cu.cm.	22.93	19.89	68.62
Distillation, % by wgt.			
270°C	7.45	9.78	0.56
271-300°C	5.44	4.41	0.08
301-360°C	6.44	7.06	0.0
361-400°C	6.36	6.80	0.0
Total	6.36	7.19	0.0
Total Percent of Variation Accounted For	83.7	64.8	79.6

Conclusions

Techniques for testing binder pitches provide very good comparisons between the properties of laboratory anode specimens and plant anodes.

Generally the apparent density and crushing strength of anodes increase, and the electrical resistivity decreases, as the softening point, coking

value, benzene and quinoline insoluble components, and specific gravity of the pitch binder increase.

Based on the multiple correlation coefficients, it was found that 83.7% of the variations in apparent density, 64.8% of the variations in electrical resistivity, and 79.6% of the variations in compressive strength of laboratory prepared and baked carbon are accounted for in the properties of softening point, coking value, benzene and quinoline insoluble components, specific gravity and distillation through 400°C.

In general, the equations presented permit predicting the apparent density, electrical resistivity, and crushing strength of laboratory anode specimens from analyses of all type pitches within the precision of the test methods for measuring the properties of the carbon.

These equations may serve as guides for laboratories without facilities for making and testing carbon anodes. They can be used by people with limited experience in appraising pitches.

TABLE III.

EQUATIONS FOR PREDICTING RESULTING PROPERTIES OF SPECIMENS OF SODERBERG COMPOSITION FROM THE CHEMICAL ANALYSIS OF THE PITCH

APPARENT DENSITY (gms./cu.cm.)	= 0.00127a + 0.00048b + 0.00121c - 0.00167d + 0.60303e - 0.16131f - 0.15269g - 0.16023h - 0.16144i + 0.15997j + 0.6684
ELECTRICAL RESISTIVITY (ohms/m./sq.mm.)	= - 0.0538a - 0.0607b + 0.3906c - 0.1309d - 77.3591e + 11.1588f + 6.8737g + 9.2822h + 9.1307i - 9.2760j + 173.277
CRUSHING STRENGTH (lbs./sq.in.)	= 8.69a - 3.93b + 14.05c - 10.75d + 17,404e - 229.06f + 85.46g - 4.61h + 36.47i - 9.47j - 16,956.95

a = softening point, °C, cube-in-air, Barrett's method D-7.
b = benzene insoluble, %, Barrett's method B-7.
c = quinoline insoluble, % Barrett's method B-21.
d = coking value, %, Conradson, 3 g. sample, A.S.T.M. D-189-46.
e = specific gravity, g./cu.cm., 25°C, Barrett's method D-4.
f = distillation fraction 0-270°C, Barrett's method C-9.
g = distillation fraction 271-300°C.
h = distillation fraction 301-360°C.
i = distillation fraction 361-400°C.
j = Total distillate, 0-400°C.

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